9th International Conference on
Instrumental **M**ethods of **A**nalysis: Modern Trends and Applications

Book of abstracts

TECHNOLOGICAL EDUCATIONAL INSTITUTE OF PELOPONNESE

20-24 September 2015
Kalamata, Greece

9th International Conference on

Instrumental Methods of Analysis: Modern Trends and Applications

IMA-2015

September 20-24, 2015, Kalamata - Greece

Organized by

Department of Food Technology,
Technological Educational Institute of Peloponnese

Laboratory of Inorganic and Analytical Chemistry,
School of Chemical Engineering NTUA

Under the auspices of

EUCHEMS Division of Analytical Chemistry

Association of Greek Chemists

Main Sponsors

ASTERIADIS

ANTISEL®
A. SELIDIS BROS SA
Authorized Distributor

PerkinElmer®
For the Better

NON SOLUS
ELSEVIER

Sponsors

RIGAS LABS
When details lead to excellence.....

HELLAMCO®
SCIENTIFIC EQUIPMENT

Interlab
Κωνσταντίνος Οικονόμου
Διεθνής Εργαστηριακός Εξοπλισμός Ε.Π.Ε.

KONSTANTOPOULOS S.A.
FOOD INDUSTRY SINCE 1956

BIOLAB

ATHENIAN BREWERY
AMSTEL Heineken open your world ΑΛΦΑ

INOMESSINIAKI Winery

Vis olivae

Supporters

European Association for Chemical and Molecular Sciences
Division of Analytical Chemistry

Association of Greek Chemists

Technological Educational Institute of Peloponnese

National Technical University of Athens

University of Ioannina

University of Patras

Aristotle University of Thessaloniki

National and Kapodistrian University of Athens

Technical University of Crete

Univeristy of Crete

Preface

The organizing committee of the IMA-2015 Conference would like to welcome all participants to the 9th International Conference on "Instrumental Methods of Analysis-Modern Trends and Applications", held in Kalamata, Greece, in September 20-24. The conference is organized by the Department of Food Technology of Technological Educational Institute of Peloponnese and the Lab of Inorganic and Analytical Chemistry of the School of Chemical Engineering of the National Technical University of Athens. IMA is a biannual series of conferences that started in 1999 and covers all areas of modern trends and applications of Chemical Analysis.

Due to the great interest and the numerous participants from the Food Science and Technology scientific community, including related companies, this year's conference will emphasize on research on Food Analysis. For this reason, four sessions on the first conference day are devoted on research related mainly to food analysis with emphasis on food safety, aroma compounds determination, packaging, and novel foods. The current analytical trends will be revealed with presentations covering a large spectrum of techniques such as Spectrochemical, Electrochemical, Chromatographic etc. The new trend of combining analytical methods and using hyphenated techniques has unfolded new perspectives and challenges in chemical analysis, dealing with difficult problems related to modern materials, food, environmental micro-pollutants of toxicological interest. These issues will also be discussed during IMA2015.

The scientific Conference program consists of 14 invited and 6 plenary lectures, 15 sessions with oral presentations and a considerable number of posters to be presented in the respective sessions. In addition, researchers of Academia, Research Institutes and the Industry will present up-to-date development on analytical instrumentation as well as applications to a wide range of physical, earth and life sciences. At the same time a cultural program with visits to archaeological sites of the Ancient Messini, the city of Kalamata and Diros cave, as well as a visit to a local oil factory will render the participants' stay more interesting and enjoyable.

We strongly believe that the discussions and the exchange of ideas among the participants during the 5 days of the meeting will make IMA a brilliant platform to initiate new research collaborations, particularly in favor of the young scientists participating in the conference.

The papers presented at IMA2015 can be submitted to 6 journals of Elsevier, depending on the topic. Accepted papers will be linked to form a Multi-journal Virtual Special Issue dedicated to IMA2015 conference.

We wish you all to enjoy this conference as all the previous IMA conferences since 1999 and have a pleasant stay in Kalamata, hoping to meet you again during the next IMA2017.

With our best regards

The Chairpersons

Dr. John Kapolos

Professor, Technological Educational Institute of Peloponnese

Dr. Maria Ochsenkühn-Petropoulou

Professor, National Technical University of Athens

Committees

International Scientific Committee

F. Adams (Univ. Antwerp), T. Albanis (Univ. Ioannina), A. Anthemidis (AUTh), O. Yavuz Ataman (METU, Ankara), J. Barek (Charles Univ., Prague), M. Beazi-Katsioti (NTUA), C. Biliaderis (AUTh), A. Bobrowski (AGH Krakow), A. Calokerinos (Univ. Athens), N. Chaniotakis (Univ. Crete), Th. Christopoulos (Univ. Patras), S. Chanthai (Khon Kaen Univ.), L. Ebdon (Univ. Bedfordshire), C. Efstathiou (Univ. Athens), A. Eroglu (Izmir Institute of Technology), L. Farmakis (Association of Greek Chemists), W. Frenzel (TU Berlin), C. Georgiou (AU Athens), S. Gücer (Uludag Univ.), E.H. Hansen (TU Lyngby), G. Hieftje (Indiana Univ.), A. Hiskia (NCSR Demokritos), G. Kakali (NTUA), I. Kalavrouziotis (HO Univ.), N. Kallithrakas-Kontos (TU Crete), S. Kamitsos (NHRF), A. Kanakis (TEI Peloponnese), J. Kapolos (TEI Peloponnese), G. Karaiskakis (Univ. Patras), M. Karayannis (Univ. of Ioannina), B. Karlberg (Stockholm Univ.), A. Kettrup (TU Munich), D. Knopp (TU Munich), A. Koliadima (Univ. Patras), M. Kompitsas (NHRF), K. Kordatos (NTUA), M. Koupparis (Univ. Athens), M. Krokida (NTUA), E. Lampi (SGCL), W. Lindner (Univ. Vienna), S. Liodakis (NTUA), R. Lobinski (Univ. Pau), G. Lymberatos (NTUA), B. Michalke (Helmholtz Center Munich), M. Mitrakas (AUTh), A. Moropoulou (NTUA), A. Moutsatsou-Tsima (NTUA), R. Niessner (TU Munich), K.-M. Ochsenkühn (NTUA), M. Ochsenkühn-Petropoulou (NTUA), V. Oreopoulou (NTUA), A. Papadopoulos (TEI Thessaloniki), I. Papadoyannis (AUTh), A. Pappa (NTUA), M. Prodromidis (Univ. Ioannina), H. Puxbaum (TU Vienna), E. Rosenberg (TU Vienna), V. Samanidou (AUTh), C. Samara (AUTh), A. Sanz-Medel (Univ. Oviedo), M. Sökmen (Karadeniz TU), I. Spiliopoulos (TEI Peloponnese), C. Stalikas (Univ. Ioannina), M. Statheropoulos (NTUA), I. Stratis (AUTh), J. Szpunar (CRNS, Pau), P. Taoukis (NTUA), N. Thomaidis (Univ. Athens), A. Tsakalof (Univ. Thessaly), A. Tsantili-Kakoulidou (Univ. Athens), F. Tsopelas (NTUA), N. Tzamtzis (NTUA), C. Tzia (NTUA), R. Tzimou-Tsitouridou (AUTh), Th. Varzakas (TEI Peloponnese), A. Vlessidis (Univ. Ioannina), A. Voulgaropoulos (AUTh), B. Welz (Univ. Federal de Santa Catarina), G. Zachariadis (AUTh)

Continuation Committee

M. Ochsenkühn-Petropoulou, NTUA (IMA 1999, 2009, 2013) M. Karayannis, Univ. Ioannina (IMA 2001), I. Stratis, AUTh (IMA 2003), N. Chaniotakis, Univ. Crete (IMA 2005), T. Christopoulos, Univ. Patras (IMA 2007), A. Calokerinos, Univ. Athens (IMA 2009), N. Kallithrakas-Kontos, TU Crete and †P. Kefalas, MAICh (IMA 2011), R. Tzimou-Tsitouridou, AUTh (IMA 2013)

Local organizers

Chairpersons

Prof. Dr. John Kapolos, Department of Food Technology, Technological Educational Institute of Peloponnese, Kalamata

Prof. Dr. Maria Ochsenkühn-Petropoulou, Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, NTUA

Members

Prof. Dimitris Velissariou (Pres. TEI Peloponnese), Dr. Lambros Farmakis (Vice Pres. Association of Greek Chemists), Prof. George Karaiskakis (Univ. Patras), Prof. Andreas Kanakis (TEI Peloponnese), Assoc. Prof. Athina Pappa (NTUA), Assoc. Prof. Roxani Tzimou- Tsitouridou (AUTh), Assist. Prof. Athanasia Koliadima (Univ. Patras), Assoc. Prof. Kostantinos Kordatos (NTUA), Assist. Prof. Ioakim Spiliopoulos (TEI Peloponnese), Dr. Klaus-Michael Ochsenkühn (NTUA), Dr. Fotis Tsopelas, Lecturer (NTUA), Dr. Konstantinos Simeonidis (AUTh), Dr. Theopisti Lymperopoulou (NTUA)

Local Organizing Committee-Secretariat

Lambros Farmakis (TEI Peloponnese), Sofia Agriopoulou (TEI Peloponnese), Anna Kostriva (TEI Peloponnese), Kallimachos Nifakos (TEI Peloponnese), John Oikonomopoulos (TEI Peloponnese), Eugenia Stamatelopoulou (TEI Peloponnese), Lambrini-Areti Tsakanika (NTUA), Angeliki Zossima (NTUA), Efthimia Kaprara (AUTh), Marianthi Malioka (AUTh)

Exhibition

Kaiti Euklidou-Tsimpogianni
Elena Ochsenkühn
Olga Serifi

General Information

Introduction

The 9th International Conference "*IMA 2015-Instrumental Methods of Analysis-Modern Trends and Applications*" 20-24 September 2015, Kalamata, Greece is a five-day scientific meeting covering all areas of modern trends and applications of Chemical Analysis. For the last 16 years IMA has provided an excellent framework for the presentation of new concepts, instruments, methods, systems, and applications in the area of modern chemical analysis. Researchers and scientists from Universities, Research Institutions, State Organizations, and the Industry come together during the meeting to present and discuss the current state of the art in the area of instrumental methods of analysis. At the same time, it provides the grounds for the graduate and post graduate students to present their projects, discuss scientific collaborations with other groups, as well as to explore employment opportunities. An exhibition of analytical instruments and accessories will be also organized in the conference place whereas a number of excursions, tours and social events are planned to be included in the program of the IMA 2015.

Topics

Current trends on Spectrochemical, Electrochemical, Chromatographic, Microscopic and Thermal analysis methods, Hyphenated techniques, Speciation analysis, Bioanalytics, Trends on sample handling and preparation, Chemical and bio-sensors, Field analysis-Mobile analytical instruments, Laboratory information management systems (LIMS), Miniaturized analytical systems (chips), Robotics and Automation, Quality control-quality assurance on analysis, Commercial developments and markets, Flow and micro-flow methodologies, Immunoassays, Electrophoretic separation techniques, Sampling techniques and strategies

Applications: Food Analysis, Environmental analysis, Biomedical (Clinical, Ecotoxicological) analysis, Pharmaceutical analysis, Material science (Nanomaterials), Archaeometry analysis, Industrial analysis.

A **special session** is going to be attributed to the applications of instrumental analytical methods on **food analysis** with emphasis to food safety, aroma compounds determination, packaging, novel foods etc.

Contributions from commercial organizations, including detailed descriptions of new instrumentation, Specific applications, Assessment of future commercial trends and opportunities.

Previous conferences

The recent past conferences were held in Chalkidiki (1999), Ioannina (2001), Thessaloniki (2003), Iraklion (2005), Patras (2007), Athens (2009), Chania (2011) and Thessaloniki (2013) with 250-300 scientific papers presented by scientists from

all over the world at each one. For the last 16 years IMA has provided an excellent framework for the presentation of new concepts, instruments, methods, systems, and applications in the area of modern chemical analysis.

Location of Conference

IMA-2015 will be held in Kalamata, Messinia prefecture at southwestern Peloponnese. Particularly, it will take place in the conference center of Elite City Resort (Navarinou 2, 24100 Kalamata) which stands next to the Messinian Bay very close to the main areas of Kalamata. Located only four (4) km away from the center of Kalamata, the transfer is easy and fast. The port of the city, is only three (3) km away, the airport of Kalamata only twelve (12) km away, thus providing for easy access to hotel's facilities. Additionally, the central bus station is just 5 km away and there are taxi services, which will accommodate you back and forth.

City of Kalamata

Kalamata is the second most populous city of the Peloponnese peninsula in southern Greece and the largest city of the homonymous administrative region. The capital and chief port of the Messenia regional unit, it lies along the Nedon River at the head of the Messenian Gulf. The history of Kalamata begins with Homer, who mentions Pharai, an ancient city built more or less where the Kalamata Castle stands today. It was believed that during ancient times the area that the city presently occupies was covered by the sea, but the proto-Greek and archaic period remains (Poseidon temple) that were unearthed at Akovitika region prove the opposite. Pharai was rather unimportant in Antiquity, and the site continued in obscurity until middle Byzantine times. Following the Fourth Crusade, Kalamata was conquered by Frankish Crusaders under William of Champlitte and Geoffrey of Villehardouin in 1205, when its Byzantine fortress was apparently in so bad a state that it could not be defended against them. Thus the town became part of the new Principality of Achaea. Kalamata was occupied by the Ottomans and Venetian Republic from 1481, like the rest of Greece until the Greek War of Independence. Kalamata was the first city to be liberated as the Greeks rose in the Greek War of Independence. On 23

March 1821, it was taken over by the Greek revolutionary forces under the command of generals Theodoros Kolokotronis, Petros Mavromichalis and Papaflessas. However, in 1825, the invading Ibrahim Pasha destroyed the city.


In independent Greece, Kalamata was rebuilt and became one of the most important ports in the Mediterranean sea. Thanks to the exploitation of the fertile Messinian lands (producing olive oil, raisins, figs etc), it developed into a wealthy urban centre and a significant port. The natural beauty of Messinia with the indented shores, sandy beaches, forested mountains and fertile valleys, coexists with significant archaeological monuments. There are numerous historical and cultural sights in Kalamata, such as the Villehardouin castle, the Ypapandi Byzantine church, the Kalograion monastery with its silk-weaving workshop where the Kalamata scarves are made, and the municipal railway park. The Church of the Holy Apostles is where Mavromichalis declared the revolt against Ottoman rule in 1821. Art collections are housed at the Municipal Gallery, the Archaeological Museum of Messenia and the Folk Art Museum.


Kalamata is located 238 km SW of Athens. Kalamata International Airport receives flights from various European destinations throughout the summer, and from various Greek cities several times a week throughout the year. The city is well connected with the rest of Greece. Buses with the KTEL bus company run frequently to a multitude of destinations throughout Greece. Kalamata is also connected to other seaside Greek cities via weekly cruise boats and ferries.

Papers presentation

Scientific program will include plenary and keynote lectures, which will provide an up-to-date presentation of modern trends of Instrumental Methods of Analysis as well as of related subjects of general interest. Invited and plenary speakers should plan on a 25 minutes long talk followed by 5 minutes of discussion. Oral Presentations: presenting authors should plan on a 12 minutes long talk followed by 3 minutes of discussion. Presentations should be in Microsoft PowerPoint format (ppt or pptx file) or Adobe Acrobat Reader format (pdf file). The file should be electronically handed by the speaker to the Registration Desk at least one session before his presentation. Contributed papers describing original research work will be also presented as posters in order to promote efficient discussion on new scientific ideas and results. The presenting authors should hang their posters in the morning, before 10 am, and remove them in the evening of the corresponding day. The preferable dimensions for posters should be 80 x 120 cm (width x height). All posters are required to conform to portrait orientation. Posters should be clear and easy to read. Type size should be sufficiently large to allow people to read from 2-3 meters.

All presentations should be in English. Poster and oral presentation will be accepted if at least one of the authors is registered and present at the conference for personal communication.

Best poster award

A competition for the best poster among the young scientists in each poster session will also take place. These awards will be given to recognize excellence in research and presentation. The winners will be announced during the Closing ceremony on 24th September at noon.

Journal publication

Participants are invited to submit manuscripts based on their presentations in one of the 6 journals (*Analytica Chimica Acta, Journal of Chromatography A, Microchemical Journal, Journal of Pharmaceutical and Biomedical Analysis, Food Chemistry, Materials Research Bulletin*), with the intention of publishing in a Multi-journal Virtual Special Issue (MJVS) that is dedicated to IMA2015 conference.

A Virtual Special Issue (VSI) is a concept which essentially rules out possible delays in publication for contributors to the special issue and will make this conference special issue more complete and accessible than it has ever been. Please see below its advantageous characteristics:

- Papers are published individually in regular journal issues at Science Direct as soon as they are accepted;
- Footnote indicating IMA-2015 conference will be included, and will link to the VSI;
- All accepted papers of the VSI will be hosted on journal homepage site of Analytica Chimica Acta – with links to the relevant papers at Science Direct;
- The VSI will include a preface, photos and/or videos, award information if any, of the conference.

Authors are suggested reading the scopes of these 6 journals carefully when selecting the best-fit journal for submission. On line submission directly to one of the above mentioned journals of MJVS with the indication “presented at IMA2015”.

Exhibition

Suppliers of analytical instrumentation and laboratory equipment will exhibit their latest offerings in the Exhibition Hall during the Conference. Official opening of the exhibition will take place on 21th September at 20:00. The exhibition area is adjacent to the lecture area and within the poster, coffee break and lunch areas in the Conference Center of Elite City Resort.

Social events

Welcome reception 20/9/2015

Elite City Resort – Pool 20:30

The Welcome Reception will be held on September 20th 20:30 at the pool area of Elite Resort Hotel.

Archaeological site of Ancient Messini 22/9/2015

Departure: Elite City Resort 08:30

The excursion to the Archeological site of Ancient Messini will take place on Tuesday's 22nd morning.

Messene is a significant ancient city in terms of its size, form, and state of preservation. It possesses not only sanctuaries and public buildings, but also imposing fortifications, and houses and tombs. It enjoys the advantage of never having been destroyed or covered by later settlements, and is located on an unspoiled inland site.

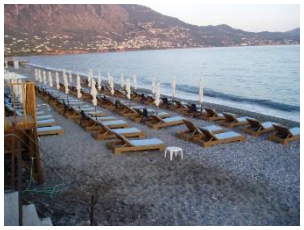
Olive Oil Factory 23/9/2015

Departure: Elite City Resort 11:30

The visit to the facilities of Konstantopoulos S.A. "OLYMP" in the area of Thourio on the north of Kalamata will take place on Wednesday's 23rd morning. The departure will be from the conference center.

Conference dinner 23/9/2015

Restaurant Trilogia 21:00



The Conference Dinner will be held on September 23rd at 21:00 in a local restaurant, **Trilogia,** located close to the seaside at a walking distance from the conference center. The menu will include a wide variety of traditional food, salads and drinks. Event will close with local traditional dances and a folklore party.

Post-conference excursion

Cave of Diros – Mani villages 24/9/2015

a minimum number of participants is required

Departure: Elite city Resort 08:30

Return: 17:30

The guided post-conference excursion to the Caves of Diros and traditional villages of Mani will take place on Friday 25th September.

The caves of Diros, are located East of Kalamata. In the three caves, a unique experience traveling barely a subterranean river length 1,600 m. The magic of the color, and the beautiful shapes, formed by the stalactites and stalagmites makes a unique spectacle.

Ticket cost to the caves entrance is not included.

Conference program

Program at a glance

Sunday 20 September 2015

16^{30}-20^{30}	Registration
18^{00}-18^{30}	Opening ceremony
18^{30}-20^{30}	Plenary lectures
20^{30}	Welcome reception

Monday 21 September 2015

08^{30}-09^{00}	Registration	
09^{00}-11^{00}	Parallel Sessions	
	Royal Cruise Hall-A	Royal Cruise Hall-D
	Food Analysis 1	Food Analysis 2
11^{00}-11^{30}	Coffee break	
11^{30}-13^{30}	Parallel Sessions	
	Royal Cruise Hall-A	Royal Cruise Hall-D
	Food Analysis 3	Food Analysis 4
13^{30}-14^{30}	Lunch	
14^{30}-15^{30}	Poster Session 1 - Exhibition	
15^{30}-17^{15}	Spectrometry 1	
17^{15}-17^{45}	Coffee break	
17^{45}-19^{30}	Electrochemistry 1	
19^{30}-21^{00}	Poster Session 1	
20^{00}	Opening of Exhibition	

Poster Session 1

Food Analysis / Spectrometry

Tuesday 22 September 2015

08^{30}-13^{30}	Visit to archaeological site of Messini	
13^{30}-14^{30}	Lunch	
14^{30}-15^{15}	Poster Session 2 - Exhibition	
15^{15}-17^{15}	Parallel Sessions	
	Royal Cruise Hall-A Mass Spectr./Chromatography 1	Royal Cruise Hall-D Mass Spectr./Chromatography 2
17^{15}-17^{45}	Coffee break	
17^{45}-19^{45}	Mass Spectrometry	
19^{45}-21^{00}	Poster Session 2 - Exhibition	

Poster Session 2

Mass Spectrometry/Chromatography

Wednesday 23 September 2015

08^{30}-09^{00}	Registration	
09^{00}-11^{00}	Parallel Sessions	
	Royal Cruise Hall-A Chromatography 1	Royal Cruise Hall-D Chromatography 2
11^{00}-11^{30}	Coffee break	
11^{30}-13^{30}	Visit to a local Olive Oil Factory	
13^{30}-14^{30}	Lunch	
14^{30}-15^{15}	Poster Session 3 - Exhibition	
15^{15}-17^{15}	Materials Science/Spectrometry 2	
17^{15}-17^{45}	Coffee break	
17^{45}-19^{15}	Archaeometry	
19^{15}-20^{15}	Poster Session 3 - Exhibition	
21^{00}	Conference Dinner	

Poster Session 3

Materials Science/Electrochemistry/Environment

Thursday 24 September 2015

09^{00}-10^{45}	Environmental Analysis
10^{45}-11^{15}	Coffee break
11^{15}-12^{30}	Electrochemistry 2
12^{30}-13^{30}	Closing Ceremony/Poster Awards

Detailed program

Sunday 20 September 2015

OPENING SESSION

(*Royal Cruise Hall-A, Chair: J. Kapolos, M. Ochsenkühn*)

18^{00}-18^{30} Greetings - Addresses

18^{30}-19^{00} Chemical imaging and analytical chemistry

IL01 F. Adams

19^{00}-19^{30} Field Flow Fractionation: A versatile technique for the separation and characterization of food macromolecules

IL02 G. Karaiskakis

19^{30}-20^{00} Analogy-based teaching in instrumental analysis

IL03 M.I. Karayannis, C.E. Efstathiou

20^{00}-20^{30} NMR methodology developments in the analysis of complex mixtures in natural products and food chemistry: From metabolomics to in-cell NMR

IL04 I.P. Gerothanassis

20^{30} ***Welcome reception***

Monday 21 September 2015

PARALLEL SESSIONS

ORAL SESSION: FOOD ANALYSIS 1

(*Royal Cruise Hall-A, Chair: D. Knopp, I. Gerothanassis*)

9^{00}-9^{30} **Analytical approaches to evaluate structure – property relations of soluble cereal fibers and their impact to food product quality and physiological functionality**

IL05 C. Biliaderis

9^{30}-9^{45} **A high-throughput SNP-genotyping method based on fluorescent microspheres for olive oil varietal identification**

MO01 D.P. Kalogianni, C. Bazakos, L.M. Boutsika, M. Ben Targem, T.K. Christopoulos, P. Kalaitzis, P.C. Ioannou

9^{45}-10^{00} **Perspectives and opportunities in plant and food science research of synchrotron microscopy and spectroscopy techniques**

MO02 D. Eichert

10^{00}-10^{15} **DNA-based meat authenticity testing by a multianalyte fluorometric method**

MO03 V.M. Myridaki, I.K. Kyriakou, D.P. Kalogianni, P.C. Ioannou, T.K. Christopoulos

10^{15}-10^{30} **Antioxidant capacity of the extracts from heather (Calluna vulgaris L. Hull) flowers**

MO04 K. Pyrzyńska, P. Dróżdż

10^{30}-11^{00} **Luminescent methods for the evaluation of antioxidant activity of olive oil and other natural products**

IL06 A.C. Calokerinos, R. Apak

11^{00}-11^{30} ***Coffee Break***

ORAL SESSION: FOOD ANALYSIS 2

(*Royal Cruise Hall-D, Chair: E. Rosenberg, L. Farmakis*)

9^{30}-9^{45} **New strategies of microbiological monitoring in food plants and water dispensers**

MO05 L. Bolelli, E. Ferri, G. Lasi, S. Gozzi, R. Moretti, S. Girotti

9^{45}-10^{00} **Development of microemulsion electrokinetic chromatography method for the analysis of illegal fat-soluble foodstuff dyes**

MO06 K. Petrů, J. Bradová, L. Pincová, M. Polášek

10^{00}-10^{15} Characterization of multifunctional Haematococcus pluvialis extracts and their application in beverage products

MO07 S. Papadaki, V. M. Christopoulou, C. Drosou, K. Tataraki, K. Kyriakopoulou, A. Pappa, M. Krokida

10^{15}-10^{30} Determination of physicochemical parameters as a function of time for physically adsorbed or chemisorbed aroma compounds on starch granules from different origin by inverse gas chromatography

MO08 K.A. Eftaxopoulou, L. Farmakis, A. Koliadima, G. Karaiskakis, J. Kapolos

11^{00}-11^{30} ***Coffee Break***

PARALLEL SESSIONS

ORAL SESSION: FOOD ANALYSIS 3

(*Royal Cruise Hall-A, Chair: C. Biliaderis, T. Varzakas*)

11^{30}-12^{00} Bioanalytical determination of mycotoxins in food samples – an overview of current concepts and trends

IL07 D. Knopp, R. Niessner

12^{00}-12^{15} Migration of specific metals in canned foods before and after opening. Validation of a new quality indicator for opened cans

MO09 G. Petropoulos, I. Passias, N. Thomaidis, C. Proestos

12^{15}-12^{30} Raman spectroscopy for the authentication of Greek extra virgin olive oil and adulteration with sunflower oil

MO10 A. Philippidis, M. Velegrakis

12^{30}-12^{45} Fatty Acids composition of Greek PDO and Traditional Cheeses, a statistical analysis on their profile acquired by a GC/FID method

MO11 G. Karanikolopoulos, L. Kioupis, K. Papadopoulou, I. Mastrantoni

12^{45}-13^{00} The application of FT-IR technique in characterizing food microencapsulation systems

MO12 C. Chranioti, A. Karamberi, L.A. Tsakanika, C. Tzia

13^{00}-13^{30} Production model and international market for Greek table olives

IL08 D. Calderon, P. Konstantopoulos

13^{30}-15^{30} ***Lunch – Poster Session 1 - Exhibition***

ORAL SESSION: FOOD ANALYSIS 4

(*Royal Cruise Hall-D, Chair: G. Karaiskakis, M. Krokida*)

12^{00}-12^{15} NMR in dairy lipid research: Improving the fatty acid profile of sheep milk by olive cake supplementation

MO13 S. Symeou, C. Papaemmanouil, C.G. Tsiafoulis, O. Tzamaloukas, D. Miltiadou, I.P. Gerothanassis

12^{15}-12^{30} Virgin Olive Oil: Examining authenticity with LC-HRMS workflows

MO14 N.P. Kalogiouri, N.S. Thomaidis

12^{30}-12^{45} Proteomic-based choice and enzyme immunoassay of mammalian muscle marker for control of meat products authenticity

MO15 E.A. Zvereva, L.I. Kovalev, A.V. Ivanov, M.A. Kovaleva, A.V. Zherdev, S.S. Shishkin, A.B. Lisitsyn, I.M. Chernukha, B.B. Dzantiev

12^{45}-13^{00} Differentiation of fresh orange juice prepared by Merlin cultivar according to geographical origin based on organic acid and sugar content using chromatographic and chemometric analyses

MO16 I.K. Karabagias, C. Nikolaou, I. Gatzias, S. Kontakos, A. Badeka, M.G. Kontominas

---

13^{30}-15^{30} ***Lunch – Poster Session 1 - Exhibition***

ORAL SESSION: SPECTROMETRY 1

(*Royal Cruise Hall-A, Chair: L. Ebdon, A. Calokerinos*)

15^{30}-16^{00} Methods to identify and conquer matrix and spectral interferences in ICP emission spectrometry

IL09 G.M. Hieftje, G. Chan, Y. Cheung, A.J. Schwartz

16^{00}-16^{15} Elemental depth profiling with nanometer resolution using a novel laboratory set-up in the soft X-ray range

MO17 J. Baumann, C. Herzog, M. Spanier, D. Grötzsch, L. Lühl, K. Witte, A. Jonas, S. Günther, F. Förste, R. Hartmann, M. Huth, D. Kalok, B. Steigenhöfer, M. Krämer, T. Holz, R. Dietsch, L. Strüder, B. Kanngießer, I. Mantouvalou

16^{15}-16^{30} Identification and quantification of six polyvinyl chloride plasticizers by proton nuclear magnetic resonance in infusion medical devices

MO18 F. Feutry, S.Genay, M.Masse, C.Barthélémy, V.Sautou, B.Décaudin, P.Odou, N.Azaroual

16^{30}-16^{45} Development of immunosensors based on optical waveguide lightmode spectroscopy (OWLS) technique for determining active substance in herbs

MO19 N. Adányi, K. Majer-Baranyi, E. Takács, B. Wang, I. Szendrő, A. Székács

16^{45}-17^{00} Chemiluminometric biosensor for genotyping of single-nucleotide

polymorphisms in methylenetetrahydrofolate reductase (MTHFR) gene

MO20 E.M. Spyrou, D.P. Kalogianni, S.S. Tragoulias, P.C. Ioannou, T.K. Christopoulos

17^{00}-17^{15} Microfluidics tubing system for mercury detection utilizing fluorescent sensor nanoparticles

MO21 J. Bell, E. Climent, M. Albrecht, K. Rurack

17^{15}-17^{45} ***Coffee Break***

ORAL SESSION: ELECTROCHEMISTRY 1

(*Royal Cruise Hall-A, Chair: M. Ochsenkühn, J. Barek*)

17^{45}-18^{15} Voltammetric sensors in stripping procedures – past and present

IL10 A. Bobrowski

18^{15}-18^{30} Adsorptive stripping voltammetry of Cr(VI) in the presence of pyrogallol red using electrodes of HgFE, BiFE and SbFE

MO22 J.M. Navia, V. Arancibia, M. Gómez, C. Rojas, C. Nuñez

18^{30}-18^{45} High sensitive determination of V(V) by catalytic adsorptive stripping voltammetry. Effect of sulfonic substituted ligand

MO23 C. Rojas-Romo, V. Arancibia

18^{45}-19^{00} How alive can electrochemical DNA biosensors be?

MO24 V. Vyskočil, Z. Krejčová, K. Stávková, and A. Hájková

19^{00}-19^{15} Development of Electrochemical Sensing Devices for Caffeine Detection and Immunosensor Applications in the Food Industry

MO25 G.F. Duffy, E.J. Moore

19^{15}-19^{30} Chalcones as multifunctional antioxidants: a study of their interaction with copper ions

MO26 O. Serifi, M. Ochsenkühn-Petropoulou, A. Karantonis, A. Detsi

19^{30}-21^{00} ***Poster Session 1 – Opening of the Exhibition***

POSTER SESSION 1

FOOD ANALYSIS / SPECTROMETRY

(*Royal Cruise Hall-B, Chair: E. Rosenberg, A. Gundlach-Graham, V. Sinanoglou, A. Vlessidis*)

P1-01 **Dispersive liquid–liquid microextraction method development for isolation and preconcentration of pesticide residues from alcoholic beverages**

M. Andraščíková, M. Brišová, S. Hrouzková

P1-02 **Analysis of volatile compounds in virgin olive oils from four cultivars using HS-SPME-GC**

C.V. Antoniou, G.C. Koubouris

P1-03 **Sugar detection in sodas utilizing a fluorescent microfluidics sensor**

J. Bell, P. Ashokkumar, M. Albrecht, K. Rurack

P1-04 **Authentication of game meat through rare earth and trace element profile: The case of Limnos island wild rabbits**

G. Danezis, A.C. Pappas, E. Zoidis, C. Papachristidis, C. Vavvas, G. Papadomichelakis, I. Hadjigeorgiou, V. Brusic, C.A. Georgiou

P1-05 **Rare earth elements & actinides accumulation patterns in game meat, backyard & commercial rabbits**

G. Danezis, A. Tsagkaris, E. Zoidis, A.C. Pappas, C. Papachristidis, C. Vavvas, G. Papadomichelakis, I. Hadjigeorgiou, V. Brusic, C.A. Georgiou

P1-06 **Monitoring of tin and aluminum release from food packaging to packaged food**

P. Diviš, P. Šiler

P1-07 **Determination of taurine in energy drink by IC/PAD**

H. Farkaš, J. Banić-Simičić, D. Ujsasi, A. Plahi Bognar, B. Marošanović

P1-08 **Sensitive determination of halogenated nitrogenous disinfection by-products in drinking water samples**

Y. Kadmi, L. Favier, M. Gavrilescu, C. Vial, D. Wolbert

P1-09 **Simultaneous determination and quantification of polyphenol compounds, flavonoids, and oleuropein derivatives using the –OH 1H-NMR spectral region: Optimization of experimental conditions and application to oregano and olive leaf extracts**

P. Charisiadis, V.G. Kontogianni, C.G. Tsiafoulis, A.G. Tzakos, I.P. Gerothanassis

P1-10 **DNA purification using a highly efficient microfluidic device with large capacity: Demonstration of DNA recovery from a few Salmonella bacteria cell lysate**

A.S. Kastania, K. Tsougeni, G. Papadakis, E. Gizeli, G. Kokkoris A. Tserepi, E. Gogolides

P1-11 Authentication tests for milk products based on a chemiluminometric hybridization assay

M. Kounelli, D.P. Kalogianni, P.C. Ioannou, T.K. Christopoulos

P1-12 Volatile compounds in probiotic dry-fermented sausages

M. Sidira, P. Kandylis, L. Bosnea, M. Kanellaki, T. Varzakas, Y. Kourkoutas

P1-13 Volatile compounds in probiotic yoghurts containing immobilized Lactobacillus plantarum 2035 on whey protein

M. Sidira, M. Kiourtzidis, N. Chorianopoulos, C. Tassou, S. Kaloutsas, G. Mitropoulou, T. Varzakas, Y. Kourkoutas

P1-14 Optimization of industrial pretreatment of Spirulina platensis cyanobacterium

S. Papadaki, K. Kyriakopoulou, M. Krokida

P1-15 Impact of feed supplementation with different natural antioxidants on fatty acid profile and color parameters of egg yolk lipid fraction

D.Z. Lantzouraki, V.J. Sinanoglou, M. Goliomytis, M. Charismiadou, S.G. Deligeorgis, P. Zoumpoulakis

P1-16 Detection of aflatoxin M1 in traditional local cheeses of Greece with a direct competitive ELISA

A. Batrinou, C. Kapsali, I. Karachristou, K. Tampratzi, D.Z. Lantzouraki

P1-17 Evaluation of the fatty acid profile in donkey's milk during lactation

Th. Massouras, G. Alexiou

P1-18 Composition, aromatic profile and coagulation properties of milk of goat graze in pasture of Algerian semi-arid areas.

Bouguerra, S. Djebili, M. Barkat, Th. Massouras

P1-19 Chemometrical development and comprehensive validation of a SPME/DI-GC-MS method for the determination of 21 important free and glycosidically bound aromatic compounds in wines. Application in Greek and international Vitis vinifera varieties

M. Metafa, Th.Varzakas, A. Vlyssides, C. Israilides, A. Economou

P1-20 Analytical challenges in investigating allergenic proteins in varieties of Solanum lycopersicum

R.T. Mócsai, A. Maczó, K. Majer-Baranyi, N. Adányi, P. Milotay, Zs. Bánfalvi, R. Tömösközi-Farkas

P1-21 Examination of bioactive components and properties of aroma in paprika powders

H. Molnár, M. Pék, R. Farkas Tömösköziné, N. Adányi

P1-22 **SERS and 2D-Fluorescence for the investigation of aminoacids and egg proteins**

A. Philippidis, Z.E. Papliaka, D. Anglos

P1-23 **A novel dispersive liquid-liquid microextraction gas chromatography-mass spectrometry method for the determination of selected biogenic amines in wine**

J. Płotka-Wasylka, J. Namieśnik

P1-24 **Microextraction in conjuction with the derivatization–strategies for the determination of BAs in wines by chromatographic techniques**

J. Płotka-Wasylka, J. Namieśnik

P1-25 **Studies on the synthesis of high added value products from Nannochloropsis oceanica using chromatographic and mass spectrometry techniques**

M.G. Savvidou, Th.V. Lymperopoulou, K.P. Balta-Brouma, M. Michailidou, K. G. Magoulas, F.N. Kolisis

P1-26 **Effect of gamma radiation on the fatty acid profiles of sesame oil**

D. Lantzouraki, P. Zoumpoulakis, I.F. Strati, G.-N. Nikolaou, S.M. Bratakos, V.J. Sinanoglou

P1-27 **Characterization of visceral oils from conventional and organically farmed Sparus aurata, Dicentrarchus labrax and Diplodus puntazzo**

V.J. Sinanoglou, D.P. Houhoula, V.R. Kyrana, V.P. Lougovois

P1-28 **Seasonal variations in the lipid and fatty acid profiles of the smooth clam Callista chione**

C. Papaioannou, V.P. Lougovois, V.R. Kyrana, I.F. Strati, V.J. Sinanoglou

P1-29 **Analysis and classification of ham meat products according to meat type and processing, using colour and texture analysis methods**

D. Xenogiannopoulos, G. Xenogiannopoulos, P. Zoumpoulakis, D. Cavouras, V.J. Sinanoglou

P1-30 **Determination of hydrolysed proteins' molecular weight in fish feeds using size exclusion chromatography and UV detection**

G. Koulis, M. Dasenaki, N.S. Thomaidis

P1-31 **Novel NMR spin- chromatography method for the identification and quantification of glutathione in white wine**

V.G. Kontogianni, C.G. Tsiafoulis, I.G. Roussis, I.P. Gerothanassis

P1-32 **Investigation on Greek white and red wines using optical absorption and Fluorescence spectroscopy in combination with Chemometrics.**

E. Poulakis, A. Philippidis, M. Velegrakis

P1-33 **Determination of quinolones in fish muscle plus skin by ultra high-performance liquid chromatography with photo–diode array detection**

V. Zonaras and Y. Kotzamanis

P1-34 **A comparative study on maternal milk's lipid composition**

G.-N. Nikolaou, V.J. Sinanoglou[1], D.Z. Lantzouraki, D. Cavouras, T. Boutsikou, D.D. Briana, A. Malamitsi-Puchner, P. Zoumpoulakis

P1-35 **Investigation of flavonoid enriched ration on chicken plasma metabolites**

C. Fotakis, P.E. Simitzis, M. Goliomytis, S.G. Deligeorgis, P. Zoumpoulakis

P1-36 **Estimating the quality of red and white meat using chemometrics on fatty acids and lipid quality indices.**

V.J. Sinanoglou, C. Fotakis, I.F. Strati, P. Zoumpoulakis

P1-37 **Spectrophotometric determination of flavonoids by formation of silver nanoparticles**

E. Terenteva, V. Apyari, S. Dmitrienko, Yu. Zolotov

P1-38 **Characterisation of Melanoidins and their metal complexes applying EPR and FTIR spectroscopic techniques**

K. Bayer, M. Kaufmann, A. Hornemann, B. Beckhoff, L.W. Kroh

P1-39 **Comparison of the scavenging activity of wines, teas and edible oils determined by the CL reaction of N,N-dimethyl-biacridylidene.**

D.C. Christodouleas, A. Calokerinos, V. Garyfali, Ch. Fotakis, K.Papadopoulos

P1-40 **Comparison of four FIA-CL methods for the evaluation of antioxidant activity of various natural products**

D.C. Christodouleas, A. Calokerinos, V. Garyfali, Ch. Fotakis, K.Papadopoulos

P1-41 **A chemiluminescent assay for the detection of allergens in foodstuffs**

S. Christopoulou, D.P. Kalogianni, S. Karaiskou, P.C. Ioannou, Th.K. Christopoulos

P1-42 **Quantitative Structure-Chemiluminescence Intensity Relationships of 4-substituted phenols acting as luminol signal enhancers**

N. Kritikos, Y.L. Loukas and Y. Dotsikas

P1-43 **Antimicrobial peptides and lipid-membranes interactions investigations in the Far-Infrared region**

A. Hornemann, D. Eichert, A. Hoehl, M. Andersch, P. Emmer, B. Tiersch, M. Ryadnov, G. Ulm, B. Beckhoff

P1-44 **The X-ray Fluorescence beamline at Elettra – Sincrotrone Trieste: new characterization opportunities for nano-structured materials**

D. Eichert, L. Luehl, F. Brigidi, A. Gambitta, W. Jark

P1-45 **Fluorescent detection of biothiols and SO_2 derivates via Michael addition reaction of it to isoxasole**

M. Gómez, M.E. Aliaga, C. Irribarren, A. Cañete, E.G. Perez

P1-46 **Formation of Au@Ag core-shell nanorods as an approach to spectrophotometric determination of catecholamines**

M. Gorbunova, L. Zamurueva, V. Apyari, S. Dmitrienko

P1-47 **Preliminary results of the chemical composition of deep sea sediments from the greater area of Santorini**

S. Foteinis, N. Kallithrakas-Kontos, C. Anagnostou

P1-48 **Sulphur Speciation by a Si-PIN X-ray detector**

N. Kallithrakas-Kontos, R. Moschochoritou

P1-49 **New possibilities for prediction of cereals' and pseudo-cereals' chemical and technological parameters by near-infrared spectroscopy**

É. Kónya, T. Halasi, P. Forgó, Zs. Cserhalmi, N. Adányi, A. Kiss

P1-50 **A new type of X-ray spectrometry UHV instruments at the SR facilities BESSY II, ELETTRA and SOLEIL**

J. Lubeck, B. Boyer, B. Detlefs, D. Eichert, R. Fliegauf, D. Grötzsch, I. Holfelder, P. Hönicke, W. Jark, R. Kaiser, B. Kanngießer, A.G. Karydas, J.J. Leani, M.C. Lépy, L. Lühl, Y. Ménesguen, A. Migliori, M. Müller, B. Pollakowski, M. Spanier, G. Ulm, J. Weser, B. Beckhoff

P1-51 **Optical waveguide lightmode spectroscopy technique-based immunosensor development for aflatoxin B_1 determination in spiced paprika samples**

K. Majer-Baranyi, Zs. Zalán, M. Mörtl, A. Székács, I. Szendrő, N. Adányi

P1-52 **The quantitative analysis of ternary mixtures of anhydrous crystalline $CaCO_3$ polymorphs using micro Raman spectroscopy**

R. Ševčík, P. Mácová, M. Pérez-Estébanez

P1-53 **Sequential injection method for determination of gamma-aminobutyric acid based on nanoparticle second order light scattering**

S. Teerasong, A. Jinnarak, D. Nacapricha

P1-54 **Multicommutation flow system for manganese speciation in water samples by solid phase extraction – flame atomic absorption spectrometry**

A. Tobiasz, M. Sołtys, D. Dudek-Adamska, S. Walas

P1-55 **Fingerprinting analysis of Romanian berries using TLC and UV-VIS spectrometry**

I.-A. Sima

P1-56 **Adulteration of extra virgin olive oils with seed oils studied with Optical Spectroscopy**

A. Papadaki, A. Philippidis, M. Velegrakis

P1-57 **Ligand-free cation-selective biomimetic sensors prepared from phospholipid-polydiacetylene mixed vesicles**

V.A. Gatselou, D.L. Giokas, G.Z. Tsogas, A.G. Vlessidis

P1-58 **Determination of dithiocarbamates with photochemically amplified chemiluminescence detection**

V.A. Gatselou, D.L. Giokas, G.Z. Tsogas, A.G. Vlessidis

P1-59 **Thiol-functionalized quantum dots as photoluminescent sensors for the determination and speciation of gold and silver nanoparticles after micelle mediated preconcentration**

G. Z. Tsogas, D. L. Giokas, A.G. Vlessidis

P1-60 **A metabolic and antioxidant profile study of herbal infusions and decoctions**

Ch. Fotakis, D. Tsigrimani, Th. Tsiaka, I. Strati, C. Makris, D. Tagkouli, Ch. Proestos, V.J. Sinanoglou, P. Zoumpoulakis

P1-61 **Determination of the Adulteration of Extra Virgin Olive Oil by Means of FTIR Spectroscopy**

E.G. Barbounis, K. Tampouris, D. Georgantas

Tuesday 22 September 2015

08^{30}-13^{30} ***Visit to archaeological site of Ancient Messini***

13^{30}-15^{15} ***Lunch – Poster Session 2 – Exhibition***

PARALLEL SESSIONS

ORAL SESSION

MASS SPECTROMETRY / CHROMATOGRAPHY 1

(*Royal Cruise Hall-A, Chair: W. Frenzel, J. Kapolos*)

15^{15}-15^{45} **ICP MS in metallomics - state-of-the-art and perspectives**

IL11 R. Lobinski

15^{45}-16^{00} **Wide-scope screening of polar emerging contaminants in environmental samples by HILIC-QToF-HR-MS/MS**

TU01 A.A. Bletsou, A.A. Markatis, P. Gago Ferrero, N.S. Thomaidis

16^{00}-16^{15} **Advanced GCMSMS analysis using a novel ionization technology and qTOF mass analyzer**

TU02 A.A. Bisi, B. M. Carola Salvi, C.A. Patkin

16^{15}-16^{30} **Volatile compounds of some aromatic plants of Algerian semi-arid' area by (HS-SPME) coupled to (GC/MS)**

TU03 A. Bouguerra, Th. Massouras, N Zouaoui, M. Barkat

16^{30}-16^{45} **Impurity profiling of meglumine by HPLC-MS**

TU04 F. Ferretti, C. Martano, L. Lattuada

16^{45}-17^{00} **NMR spin- chromatography in dairy lipid research**

TU05 C. Papaemmanouil, S. Symeou, C.G. Tsiafoulis, D. Alivertis, O. Tzamaloukas, D. Miltiadou, A.G. Tzakos, and I.P. Gerothanassis

17^{00}-17^{15} **Design characteristics of a post-column derivatization system for tetradotoxin analysis**

TU06 D. Tanis, P. Vareltzis, G. Nikolaides and P.G. Rigas

17^{15}-17^{45} ***Coffee Break***

ORAL SESSION

MASS SPECTROMETRY / CHROMATOGRAPHY 2

(*Royal Cruise Hall-D, Chair: A. Sanz-Medel, N. Kallithrakas*)

15^{45}-16^{00} HPLC profiles of phenolic compounds present in olive oil by-products extracts

TU07 S. Chanioti, P. Siamandoura, C. Tzia

16^{00}-16^{15} Investigation of the Cr(VI) behavior in foods by HPLC – ICP MS

TU08 V. Vacchina, I. de la Calle, F. Séby

16^{15}-16^{30} The use of immobilized artificial membrane chromatography for modelling bioconcentration of pharmaceutical compounds in the environment

TU09 F. Tsopelas, C. Stergiopoulos, A. Tsantili- Kakoulidou, M. Ochsenkühn-Petropoulou

16^{30}-16^{45} Multianalyte assay for prostate cancer-related gene quantification by hybridization on fluorescent microspheres

TU10 I.K. Kyriakou, K. Mavridis, D.P. Kalogianni, P.C. Ioannou, T.K. Christopoulos, A. Scorilas

16^{45}-17^{00} The comparison of Capillary Electrophoresis and Ion Chromatography with Electrospray Ionization-Mass Spectrometry methods for thermal stability studies on ionic liquids

TU11 M. Pyschik, M. Winter, S. Nowak

17^{00}-17^{15} Conformational characterization of polyelectrolyte complexes using Ion Mobility-Mass Spectrometry

TU12 M. Atakay, C. Wesdemiotis, B. Salih

17^{15}-17^{45} ***Coffee Break***

ORAL SESSION: MASS SPECTROMETRY

(*Royal Cruise Hall-A, Chair: J. Szpunar, N. Thomaidis*)

17^{45}-18^{15} Novel Plasma-MS instrumentation for P- and S- guided targeted proteomics and nm-scale depth-profile solid analysis

IL12 S. Diez Fernández, J. Ruiz Encinar, A. Sanz-Medel

18^{15}-18^{30} Using Ambient Mass Spectrometry source for the analysis of nanometer thick organic layers in nanoparticle.

TU13 A.A. Bisi, S. Reddy

18^{30}-18^{45} Investigation of single-particle ICP-TOFMS as a tool for comprehensive sizing and counting of mixtures of engineered nanoparticles

TU14 A. Gundlach-Graham, A. Praetorius, J. Navratilova, B. Ramkorun-Schmidt, F. von der Kammer, D. Günther

18^{45}-19^{00} Development of isolation of psychoactive compounds from plants using the microwave- and ultrasound-assisted extraction techniques

TU15 M. Woźniakiewicz, J. Nowak, M. Ciechomska, A. Woźniakiewicz, P.Kościelniak

19^{00}-19^{15} Wide-scope QSRR models to support suspect and non-target screening of polar compounds in HILIC - ESI(+) - LC-HRMS

TU16 R. Aalizadeh, N.S. Thomaidis

19^{15}-19^{45} Combined speciation techniques proof changes in the metallome and metabolome as a cause for transition-metal related neurodegeneration

IL13 B. Michalke, K. Neth

19^{45}-21^{00} ***Poster Session 2 – Exhibition***

POSTER SESSION 2

MASS SPECTROMETRY / CHROMATOGRAPHY

(*Royal Cruise Hall-B, Chair: M. Woźniakiewicz, R. Aalizadeh, Th. Lymperopoulou, C. Tsiafoulis*)

P2-01 **Two Temperature Sorption Strategy for Screening of Volatile Compounds in Barley and Wheat Malts by Method Based on Solid Phase Microextraction**

M. Adam, A. Eisner, K. Adámková, P. Bajerová, K. Ventura

P2-02 **A HPLC-MS/MS Method for the accurate quantification of Cyclopiazonic Acid using stable isotope as Internal Standard**

P. Ansari, G. Häubl

P2-03 **Trace elements in beers from Greek microbreweries by ICP-MS**

E. Bempi, S. Karavoltsos, A. Sakellari, A. Kaliora, E. Dassenakis, N. Kalogeropoulos

P2-04 **Application of dynamic headspace and GC-MS technique for the determination of oxygenated volatile organic compounds in industrial wastewater**

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, A. Fernandes

P2-05 **Studies of VOC degradation using Advanced Oxidation Processes (AOP) by means of "GREEN" extraction method and GC-MS technique**

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, A. Fernandes

P2-06 **Matrix solid-phase dispersion for the determination of antidepressants and antipsychotics in human hair by LC- Hybrid LTQ Orbitrap MS**

E. Trantopoulos, V. Boti, V. Boumba, T. Albanis

P2-07 **In-tube roasting combined with GC-MS profiling as new approach to evaluate the aroma potential of Tanzanian cocoa beans**

A. De Winne, J. Van Durme

P2-08 **Development and validation of a novel LC-MS/MS method for the quantitative determination of brinzolamide in dried blood spots**

A. Foivas, Y. Dotsikas, A. Malenović, N. Kostić, M. Božić, M. Knežević, Y.L. Loukas

P2-09 **Inductively Coupled Plasma-Mass Spectrometric analysis as a tool for Rare Earth Elements analysis: A case study on mineral processing of REE ores**

V. Angelatou, N. Xirokostas N., C.-A. Drosou, E.I.P. Drosos, D. Eliopoulos

P2-10 **Qualitative analysis of compounds in commercial fragrance mixture of essential oils (Rose Josephine) for preparation of the perfume using gas chromatography-mass spectrometry**

S. Surmová, A. Eisner, M. Adam, P. Bajerová, T. Bajer K. Ventura

P2-11 **Highly efficient sample preparation and quantification of N-nitroso compounds in water samples using solid-phase extraction and ultra-performance liquid chromatography-tandem mass spectrometry**

Y. Kadmi, L. Favier, A. I. Simion, D. Wolbert

P2-12 **Improving the quality characteristics of marc spirits produced by adding dried figs**

P. Giannouzi, P. G. Demertzis, K. Akrida-Demertzi

P2-13 **Development of a sample preparation method for manganese speciation in plant**

E. Grygo-Szymanko, A. Tobiasz, A. Wisłocka, D. Dudek-Adamska, N. Miliszkiewicz, S. Walas

P2-14 **Early identification of etiological agents of fungal infection and assessment of susceptibility antifungal drug, amphotericin B, by advanced separation techniques in human blood**

M. Horká, K. Šlais, J. Šalplachta, F. Růžička, M. Tesařová, P. Karásek, M. Roth

P2-15 **Determination of multiclass pesticides in water samples combining Solid Phase Extraction (SPE) coupled to GC-MS and LC-MS. A case study: Louros River (N.W. Greece)**

M. Kapsi, Ch. Tsoutsi, T. Albanis

P2-16 **Determination of various pesticides in fresh waters by means of high resolution & high mass accuracy hybrid linear ion - trap - orbitrap mass spectrometry**

Ch. Nannou, V. Boti, M. Tsomi, G.Patakioutas, T. Albanis, G. Karras

P2-17 **Effect of the addition of berries in the antioxidant capacity of traditional Greek spirits**

A.K. Kosma, P.G. Demertzis. K. Akrida-Demertzi

P2-18 **MALDI-TOF MS in identification and discrimination of *Staphylococcus aureus* strains**

J. Šalplachta, F. Růžička, M. Horká

P2-19 **Analysis of glycoconjugates from primary brain tumors using a complex mass spectrometric methodology**

A.F. Serb, L. Bozin, A. Dema, M. Georgescu, E. Sisu, A.D. Zamfir

P2-20 **Correlations between arsenolipids, organic and inorganic forms of arsenic, mercury and selenium in muscles and cephalothoraxes of *Aristaeomorpha foliacea* shrimp.**

G. Soultani, V. Sele, R.R. Rasmussen, I. Pasias, E. Stathopoulou, N. Thomaidis, M. Scoullos, J.J. Sloth

P2-21 **Determination of fatty acids and trace elements in muscles and cephalothoraxes of a Mediterranean red shrimp**

G. Soultani, E. Stathopoulou, M. Kostakis, N. Thomaidis, M. Scoullos, C. Jacobsen, J.J. Sloth

P2-22 **Preparation and evaluation of matrix-matched standards towards analysis of distribution of elements in historical bones by laser ablation inductively coupled plasma mass spectrometry**

S. Walas, N. Miliszkiewicz, A. Tobiasz, E. Grygo-Szymanko

P2-23 **UHPLC-MS/MS quantitative profiling of tryptophan related neuroactive substances in human serum and cerebrospinal fluid**

E. Hényková, H. Přikrylová Vránová, P. Amakorová, T. Pospíšil, A. Zukauskaite, M. Vlčková, L. Urbánek, O Novák., P. Kaňovský, M. Strnad

P2-24 **MAE/UHPLC-TOF-MS as a method for determination of carbamazepine and its metabolite in autopsy materials**

S. Lendor, P. Kościelniak, R. Wietecha-Posłuszny, A. Woźniakiewicz, M. Zawadzki

P2-25 **Simultaneous quantitative determination of allergic ingredients in oxidative hair dyes**

J.H. Ahn, R.Y. Kim, C.W Park

P2-26 **Novel bitumen derived stationary phases for gas chromatography**

G. Boczkaj, M. Momotko, D. Chruszczyk, P. Makoś

P2-27 **Application of monolithic material for determination of iohexol in serum samples by capillary liquid chromatography**

P. Chaisuwan, T. Chaloemsuwiwattanakan, D. Nacapricha, P. Wilairat

P2-28 **Development of an automated method for methylxanthines determination by gradient–elution flow–injection chromatography**

P. Chorti, A. Economou

P2-29 **Development and validation of a low–pressure chromatography method for the rapid determination of 4 parabens in cosmetic products**

M. Barbatsi, P. Chorti, A. Economou

P2-30 **Simultaneous capillary electrophoretic analysis of inorganic anions and cations in sweat samples as a novel approach in cystic fibrosis diagnosis**

P. Ďurč, M. Greguš, F. Foret, J. Skřičková, E. Pokojová, L. Homola, M. Dastych, H. Vinohradská, P. Kubáň

P2-31 **Novel portable capillary electrophoretic instrument for analysis of very small samples and its application in the analysis of exhaled breath condensate.**

M. Greguš, F. Foret, P. Kubáň

P2-32 **A new capillary electrophoretic method for determination of oxidized and reduced glutathione in non-invasively acquired biological samples**

J. Hodáková, J. Preisler, F. Foret, P. Kubáň

P2-33 **C-reactive protein in viral and bacterial infections**

R.F. Mătieş

P2-34 **Chiral Amino Acid Ester-Based Ionic Liquids: Their Utility as Additives in Capillary Electrophoresis for Improved Chiral Separations**

M. C. Mavroudi, C.P. Kapnissi-Christodoulou

P2-35 **Determination of boiling point distribution by means of chromatographic techniques - standard test methods and new developments**

M. Momotko, D. Chruszczyk, P. Makoś, G. Boczkaj

P2-36 **Multi-applicational character of silanized silica gel as stationary phase for gas chromatography**

M. Momotko, P. Makoś, D. Chruszczyk, G. Boczkaj

P2-37 **Application of Hydrophilic Interaction Liquid Chromatography (HILIC) in the Separation and Analysis of Cathinone Regio-Isomers using HPLC**

E.Y. Santali, D.G. Watsona, O.B. Sutcliffe

P2-38 **Modern Separation of Liposolubile Vitamins in Clinical Research**

D. Solichová, L. Kujovská Krčmová, J. Plíšek, J. Aufartová, E. Kasalová, B. Honegrová, P. Solich

P2-39 **An improved QSAR model for explaining the blood–brain barrier permeability mechanisms**

R. Aalizadeh, N.S. Thomaidis

P2-40 **Magnetic solid phase extraction based on magnetic hypercrosslinked polystyrene for determination of tetracycline antibiotics in waters with HPLC**

V.V. Tolmacheva, E.V. Kochuk, V.V. Apyari, S.G. Dmitrienko

P2-41 **Optimization of a RP-HPLC/UV-Vis technique for the separation of the individual heavy and light rare earths from red mud after selective extraction/backstripping processes**

L.-A. Tsakanika, M. Ochsenkühn-Petropoulou

P2-42 **Efavirenz determination in samples obtained in transport studies using HPLC with UV detection**

L. Zelena, J. Reznicek, M. Ceckova, H. Sklenarova

P2-43 **Development and validation of HPLC methods for the determination of amino acids in pharmaceutical formulation based on precolumn derivatization and Vis detection and ion-exchange separation and chemiluminescence detection**

D.C. Tsikna, A. Economou, M. Koupparis

P2-44 Fat droplets characterization of synthetic milk emulsions at various casein concentrations (Cas), by the SdFFF method

A. Vagena. G. Karaiskakis, J. Kapolos, A. Koliadima

Wednesday 23 September 2015

PARALLEL SESSIONS

ORAL SESSION: CHROMATOGRAPHY 1

(*Royal Cruise Hall-A, Chair: B. Michalke, A. Pappa*)

9^{00}-9^{30} **Comprehensive Two Dimensional Liquid Chromatography – Coming of Age?**

IL14 E. Rosenberg

9^{30}-9^{45} **Potential of capillary electrophoresis in clinical diagnosis and monitoring**

WE01 P. Kubáň

9^{45}-10^{00} **Cadmium and mercury speciation in water hyacinth using HPLC-ICP-AES based approach**

WE02 T.E. Romanova, O.V. Shuvaeva

10^{00}-10^{15} **Measurement of acid-soluble aldehydes and alcohols derived from lignin using HPAEC-PAD**

WE03 N. Anders, H. Humann, A. C. Spieß

10^{15}-10^{30} **Application of analytical distillation tools for the sample production of lube base oil**

WE04 A. George, M. Berthod, N. Chandak, M. Nasser Al Shebli

10^{30}-11^{00} **Membrane-based sample preparation techniques for chromatographic analysis**

IL15 W. Frenzel

11^{00}-11^{30} ***Coffee Break***

ORAL SESSION: CHROMATOGRAPHY 2

(*Royal Cruise Hall-D, Chair: R. Lobinski, M. Karayannis*)

9^{30}-9^{45} **Incurred Sample Reanalysis: Considerations on the novel regulatory requirement in bioanalysis**

WE05 Y. Dotsikas

9^{45}-10^{00} **3 Years of stirring-assisted lab-in-syringe: Development, applications, and potentials**

WE06 B. Horstkotte, P. Solich

10^{00}-10^{15} **Fast method for the determination of residual solvents in**

radiopharmaceutical products

WE07 M. Mihon, C. Tuta, A.C. Ion, D. Niculae, V. Lavric

10^{15}-10^{30} Different approaches to determination of acid dissociation constants of warfarin and hydroxywarfarins using capillary electrophoresis

WE08 M. Woźniakiewicz, P. Nowak, M. Mitoraj, P. Olechowska, P. Kościelniak

11^{00}-11^{30} ***Coffee Break***

11^{30}-13^{30} ***Visit to a local Olive Oil Factory***

13^{30}-15^{15} ***Lunch – Poster Session 3 – Exhibition***

ORAL SESSION: MATERIALS SCIENCE / SPECTROMETRY 2

(*Royal Cruise Hall-A, Chair: G. Hieftje, F. Adams, A. Koliadima*)

15^{15}-15^{45} Materials characterization at the nanoscale by X-ray spectrometry

IL16 B. Beckhoff, P. Hönicke, I. Holfelder, J. Lubeck, M. Müller, A. Nutsch, B. Pollakowski, C. Streeck, R. Unterumsberger, J. Weser

15^{45}-16^{00} Optimizing biosensors labels components and their discrimination efficiency using SEIRA methodology

WE09 A. Hornemann, D. Eichert, S. Flemig, G. Ulm, B. Beckhoff

16^{00}-16^{15} Surface functionalization of sol-gel grown NiO thin films by Palladium nanoparticles for Hydrogen gas sensing

WE10 I. Sta, M. Jlassi, M. Kandyla, M. Hajji, P. Koralli, M. Kompitsas, H. Ezzaouia

16^{15}-16^{30} Hydration study of oil well cements and the relation with their chemical and physical characteristics

WE11 D. Velissariou, N. Katsiotis, P. Tsakiridis, M. Beazi-Katsioti

16^{30}-16^{45} Synthesis and characterization of Paramagnetic Fe_3O_4 nanoparticles @ graphene oxide nanohybrid material

WE12 D. Karampatsos, A. Ntziouni, G. Efthymiou, K. Fujisawa, M. Terrones and K. Kordatos

16^{45}-17^{15} Atomic fluorescence spectroscopy – analytical curiosity or useful tool

IL17 L. Ebdon

17^{15}-17^{45} ***Coffee Break***

ORAL SESSION: ARCHAEOMETRY

(*Royal Cruise Hall-A, Chair: B. Beckhoff, K. Ochsenkühn*)

17^{45}-18^{15} Tales of Archaeometry from Anatolia

IL18 O.Y. Ataman, Ü. Muşkara, M. Aydın

18^{15}-18^{45} Contribution of analytical chemistry in environmental and cultural physical sciences

IL19 J.A. Stratis, H. Hasa, M.H. Mahmoud , C. Makarona, E. Daftsis, N. Kantiranis, El. Charalampous, A.C. Charalambous, D.N. Papadopoulou, A.M.A. Mousa, N. Tsirliganis

18^{45}-19^{15} The use of instrumental analysis for investigations in archeology and history of arts: Some cases with exceptional interest for the society

IL20 M.I. Karayannis

19^{15}-20^{15} ***Poster Session 3 –Exhibition***

21^{00} ***Conference Dinner***

POSTER SESSION 3: MATERIALS SCIENCE ELECTROCHEMISTRY/ENVIRONMENT

(*Royal Cruise Hall-B, Chair: K. Kordatos, D. Eichert, F. Tsopelas, L. Tsakanika*)

P3-01 **Graphene oxide-based sensing system for detection of double-stranded DNA**

A. Giannakopoulos, I.K. Kyriakou, D. Tasis, D.P. Kalogianni, K. Papagelis, P.C. Ioannou, Th.K. Christopoulos

P3-02 **Formation of graphene nanosheets from graphene oxide thin films via one-step heat treatment**

D. Karampatsos, A. Ntziouni, G. Efthymiou, K. Kordatos

P3-03 **Selective fractionation of crude oil by means of separation techniques for analytical and preparative applications – a case of asphaltenes**

M. Momotko, D. Chruszczyk, P. Makoś, G. Boczkaj

P3-04 **Determination of thiocyanate and other inorganic ions in placenta samples**

S. Narkowicz, Ż. Polkowska, B. Kiełbratowska, J. Namieśnik

P3-05 **Incorporation of endogenous olive oil compounds in olive oil w/o food nanoemulsions without co-surfactant and study of their properties and stability**

M. Katsouli, V. Polychniatou, C. Tzia

P3-06 **Nanomaterials characterization by DLS, AF4-MALLS and SP-ICP-MS in consumer products**

I. De La Calle, M. Menta, M. Klein, V. Vacchina, F. Séby

P3-07 **Identification of superior ethanol tolerant industrial yeasts using droplet microfluidics**

Y. Vervoort, R.S. Wiederkehr, T. Stakenborg, P. Fiorini, L.Lagae, K.J. Verstrepen

P3-08 **A study of the determination of Co(II) by adsorptive stripping voltammetry at disposable screen–printed electrodes modified with a Bi precursor**

M. Maczuga, A. Economou, A. Bobrowski, M. Prodromidis

P3-09 **Application of monolithic material for determination of iohexol in serum samples by capillary liquid chromatography**

P. Chaisuwan, T. Chaloemsuwiwattanakan, D. Nacaprich, P. Wilairat

P3-10 **Microfluidic device integrated with screen printed graphene based-electrochemical sensor for glutathione detection**

C. Karuwan, W. Pimpao, A. Wisitsoraat, T. Maturos, P. Chaisuwan, D. Nacapricha, A. Tuantranont

P3-11 **Determination of Sudan I in the presence of Sunset Yellow by adsorptive stripping voltammetry**

M. Gómez, V. Arancibia, C. Rojas M.E. Aliaga

P3-12 **Study of the Interaction of 4-Nitrobiphenyl with DNA at a Hanging Mercury Drop Electrode**

E. Horakova, V. Vyskocil, J. Barek

P3-13 **Electrochemical biosensors based on minireactors with various types of amalgam and silica powders for flow systems**

O. Josypčuk, B. Josypčuk

P3-14 **Application of the general system of phenomenological peak models construction**

S.V. Romanenko, E.V. Larionova

P3-15 **Potentiometric biosensing applications using lab-made electrochemical sensors based on lipid stabilized films in contact with two different nano-electrodes**

G.-P. Nikoleli, V.N. Psychoyios, N. Tzamtzis, T. Varzakas

P3-16 **Effect of pyrrolidine dithiocarbamate and diethyl dithiophosphate on the determination of arsenic by adsorptive stripping voltammetry**

C. Núñez, V. Arancibia

P3-17 **Chiral Cavity Ring-Down Polarimetry: New methods for ultrasensitive measurements of chirality**

A. Papadaki, D. Sofikitis, A. Spiliotis, G. Katsoprinakis, B. Loppinet, T.P. Rakitzis

P3-18 **Acid-base properties of the pH indicators into polymethacrylate matrix**

N. Gavrilenko, N. Saranchina, A. Sukhanov, I. Mikheev, M.Proskurnin

P3-19 **The transparent of optical sensors PEG-PMMA on xanthene dyes**

N. Gavrilenko, N. Saranchina, M. Gavrilenko

P3-20 **Monitoring methodology of selected groups of VOCs in industrial wastewater – a review**

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, A. Fernandes

P3-21 **The potentialities of atomic absorption techniques based on the high-resolution continuous source for environmental analysis**

M.Yu. Sinitsyn, A.G. Borzenko

P3-22 **Continuous measurement of water soluble components of atmospheric aerosols**

P. Mikuška, L. Čapka, A. Kořínková, Z. Večeřa

P3-23 **A Portable device for fast analysis of explosives in the environment**

L. Čapka, Z. Večeřa, P. Mikuška, J. Šesták, V. Kahle, A. Bumbová

P3-24 **Influence of surface tension of simulated pulmonary fluids on bioavailability of metals in urban aerosol and vehicle exhaust**

P. Coufalík, P. Mikuška, K. Křůmal, M. Vojtíšek, T. Matoušek, Z. Večeřa

P3-25 **A universal analyzer for large volume preconcentration of nanomolar iron(ii) from seawater on renewable sorbent**

B. Horstkotte, P. Chocholouš, P. Solich\

P3-26 **Optimizing the determination of antimony, arsenic and chromium in drinking water by graphite furnace atomic absorption spectrometry**

N. Tziarou, E. Kaprara, M. Mitrakas

P3-27 **Application of in-situ passive flux samplers (PFSs) in the field of estimating the emission flux of volatile organic compounds emitted from laminated wood-based materials and floor coverings**

M. Marć, J. Namieśnik, B. Zabiegała

P3-28 **The estimation of total volatile organic compounds emissions generated from peroxide cured natural rubber/polycaprolacone blends**

K. Formela, M. Marć, J. Namieśnik, B. Zabiegała

P3-29 **Tar composition in biogas depending on gasification conditions**

S. Osipovs

P3-30 **Determining the isotopic composition of nitrate in sediments in the gulf of Riga**

S. Osipovs, A. Skute, D. Vardanjans

P3-31 **Heavy metal pollution of pond sediments**

K.S. Patel, N.S. Dahariya, Y. Nayak, N.K. Jaiswal, L. Matini, L. Borgese, A. Gianoncelli, E. Bontempi

P3-32 **Investigation of the adsorption of gaseous pollutants into various aquatic environments at different temperatures**

D. Sevastos, A. Koliadima

P3-33 **New environmental and biological reference materials for persistent organic pollutants such as PAHs and PCBs compounds**

M. Słomińska, B. Zabiegała, G. Bajger-Nowak, M. Marć, P. Konieczka, J. Namieśnik

P3-34 **Determination of lead in drinking water: Exploring the potential of in-syringe analysis for automation of direct-immersion single-drop microextraction**

I. Šrámková, B. Horstkotte, K. Fikarová, H. Sklenářová, P. Solich

P3-35 **Automated control monitoring of the content of pH, Cl^--, NO_3^-- ions in the wastewater by ionometry**

A.G. Kagirov, A.N. Vtorushina, D.A. Kalashnikova

P3-36 **Solid phase extraction of lead by a nanosized urchin-like $NiCo_2O_4$ adsorbent prior to determination FAAS**

E. Yavuz, Ş. Tokalıoğlu, H. Şahan, Ş. Patat

P3-37 **Separation and pre-concentration of beryllium from street sediment and water samples by tannic acid functionalised graphene aerogel prior to GFAAS determination**

E. Yavuz, Ş. Tokalıoğlu, H. Şahan, Ş. Patat

P3-38 **Automation of drug transport monitoring using sequential injection manifold**

L. Zelená, E. Lopes, M. Segundo, M. Miró, L. Hyršová, P. Pávek[5], H. Sklenářová

P3-39 **Physical and Chemical Characteristics of a typical Greek Refuse Derived Fuel**

D. Bakirtzis, P. Danias, C. Michalopoulos, V. Tsapara and S. Liodakis

P3-40 **The effects on auto-ignition of Petcoke mixtures with Refuse Derived Fuel**

D. Bakirtzis, P. Danias, V. Tsapara, C. Michalopoulos and S. Liodakis

P3-41 **Assessment of the synergistic fire-retardant effect of a new gel-carbonate mineral mixture in a large-scale test**

D. Bakirtzis, V. Tsapara, D. Vorisis, S. Liodakis and P. Joseph

Thursday 24 September 2015

ORAL SESSION: ENVIRONMENTAL ANALYSIS

(*Royal Cruise Hall-A, Chair: O. Ataman, J. Stratis*)

9^{00}-9^{15} **New matrix - free reference materials in the form of optical fibers for benzene and toluene analysis**

TH01 M. Słomińska, P. Konieczka, J. Namieśnik

9^{15}-9^{30} **A joint research project for the production and certification of matrix reference materials for environmental analysis**

TH02 A. Isleyen, J. Vogl, N. Scrundric, A. Jotanovic, T. Näykki, M. Horvat, A. Zoń, E. Bulska, M. Ochsenkuhn- Petropoulou, S.Z. Can, M. Bilsel, K. Hafner, N. Perkola, B. Ari, M. Tunç, B. Binici

9^{30}-9^{45} **Phase ratio variation approach to quantify adsorption behavior of volatile organic compounds in Nalophane sampling bags**

TH03 J. Van Durme

9^{45}-10^{00} **PM10 emissions: The importance of biomass type and combustion conditions**

TH04 A. Zosima, M. Ochsenkühn-Petropoulou

10^{00}-10^{15} **Decision making in sewage sludge management**

TH05 M. Malioka, E. Darakas, A. Kungolos and D. Latinopoulos

10^{15}-10^{30} **Influence of elevated pH and strong organic load presence on Granular Activated Carbon's bromate removal ability**

TH06 F.A. Megalopoulos, M.T. Ochsenkühn-Petropoulou

10^{30}-10^{45} **Optimizing magnetic nanoparticles for drinking water technology: The case of Cr(VI)**

TH07 E. Kaprara, M. Mitrakas, N. Andritsos and K. Simeonidis

10^{45}-11^{15} ***Coffee Break***

ORAL SESSION: ELECTROCHEMISTRY 2

(*Royal Cruise Hall-A, Chair: A. Bobrowski, F. Tsopelas*)

11^{15}-11^{30} **Non-traditional electrode materials for voltammetric and amperometric monitoring of biologically active organic compounds**

TH08 J. Barek, J. Fischer, J. Wang

11^{30}-11^{45} **A new electrochemical approach for determination of antihypertensives in pharmaceuticals and biological samples based on boron-doped diamond sensor**

TH09 K. Cinková, Ľ. Švorc

11^{45}-12^{00} New method for glass electrode internal calibration in the determination of functional groups of humic substances

TH10 I. Boal-Palheiros

12^{00}-12^{15} Derivative spectroscopic determination of enrofloxacin in some natural samples

TH11 Ch.M. Rashid, N.A. Fakhre, U.K. Ahmed

12^{15}-12^{30} A novel respirometer for determination of compost stability

TH12 C. Tsiodra, A. G. Vlyssides

12^{30}-13^{30} ***Closing ceremony – Poster awards***

Sunday 20 September 2015

Royal Cruise Hall-A

Chair: J. Kapolos, M. Ochsenkühn-Petropoulou

Opening Session

Invited lecture

Chemical imaging and analytical chemistry

F. Adams

University of Antwerpen, B-2610 Wilrijk, Belgium

Email: freddy.adams@uantwerpen.be

IL01

Over the last 50 years, different analytical methods were developed and refined to link the composition and structure of man-made and natural materials at the nano/micro scale to their functional behavior at the macroscopic scale. These developments came at the price of increasingly complex analytical equipment and procedures of analysis. They also gave rise to a vast increase of information on each element of a 2-D or a 3-D data array resulting from a systematic set of measurements. In these arrays, each individual element thus becomes a complex integrated set of morphological, structural and compositional information.
With imaging analysis and other analytical methodologies that produce massive amounts of data, analytical chemistry is increasingly transformed from a hypothesis-driven targeted methodology into a discovery-driven, shotgun methodology. In the non-targeted approach one must decide what needs to be measured, the method should be selected and validated and the analysis performed. In a non-targeted approach everything feasible is determined and information is extracted from the collected data. In such conditions, the central concept –the essence- of analytical chemistry and its relation to standard metrological concepts (uncertainty, validation, and/or traceability to fundamental standards…) seems to lose its central guiding role. While in common applications analytical chemistry relies on the production of quantitative and accurate data, in imaging applications there is a need for increasingly complex data evaluation tools based on reliable statistical and chemometric methods.

Invited lecture

Field Flow Fractionation: A versatile technique for the separation and characterization of food macromolecules

G. Karaiskakis

Department of Chemistry, University of Patras, GR-26504 Patras, Greece

E-mail: G.Karaiskakis@chemistry.upatras.gr

IL02

Field – Flow Fractionation (FFF) is a one-phase chromatographic system in which the stationary phase is replaced by an external field applied perpendicular to the direction of the carrier liquid.

Each field type corresponds to a distinct subtechnique of FFF. In practice, by now have been developed four such subtechniques of FFF. The **Sedimentation FFF** (SdFFF), which uses a lateral centrifugal or gravitational field, the **Flow FFF** (FlFFF) in which the lateral force is caused by a second solvent stream moving across the channel thickness through semipermeable upper and lower channel walls, the **Thermal FFF** (ThFFF), which is based on a temperature gradient formed in a channel between hot and cold metal bars and the **Electrical FFF** (ElFFF), which depends on electrical potential differences applied across a channel having semipermeable walls to prevent ion accumulation. **Steric FFF** (StFFF), which is the limiting form of FFF discussed earlier for large particles, can operate with any of the forces above.

From all the subtechniques of FFF mentioned above the most applicable to the food separation and characterization are the SdFFF and the FlFFF, and especially the asymmetrical flow FFF (AF4).

SdFFF as well as AF4 are two of the few separation methods that are well suited for the analysis of food macromolecules, like starches from different origin due to their polydispersity and large scale, dairy and cereal proteins, cellulose derivatives, alginate and carrageenan polysaccharides, etc.

Recent years the efforts of researchers working on FFF are also focused on the separation and characterization of nanoparticles in food contact materials or complex food matrices.

Acknowledgment

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: ARCHIMEDES III. Investing in knowledge society through the European Social Fund.

Invited lecture

IL03

Analogy-based teaching in instrumental analysis

M.I. Karayannis[1] and C. E. Efstathiou[2]

[1] University of Ioannina, Dept. of Chemistry
[2] National Kapodistrian University of Athens, Dept. of Chemistry

E-mail: mkaragia@cc.uoi.gr

Analogies provide to teachers with a tool that appeal to real life examples and student's daily experience. Students are aided by analogies to understand certain science concepts and phenomena, from a field of science, which are either not directly observable, or even easy to imagine them. Students can compare them with pictures or with something that is observable or with a concept they are familiar and is more understandable.

Specifically in chemistry, analogical demonstrations are very useful teaching tools, for both teachers and students, because this field of science includes many abstract concepts and reasoning to different theoretical approaches. Such concepts and phenomena include: resonance, intermediate and transition complex in reaction mechanisms, chemical equilibria, collision theory, theories of chromatographic separations, the variation of atomic sizes in the periodic table, functional groups, resonance structures, polarizability and ionization of atoms and molecules, differences in reactivity between alkyl and vinyl halides, S_N1 and S_N2 mechanisms, theories of buffer solutions, mechanisms of the formation of precipitates, the concept of the environmental stress, sensitivity-response time-selectivity-noise- limit of detection of chemical- and bio-sensors, the concept of capacity (electrical, thermal, environmental, spatial, etc.), and so on. .

Of course, analogies have their limitations and we must keep in mind that students may develop misconceptions from analogies. only, if students understand the target concept and the analogy, they will be able to identify such limitations.

For example, periodic variation of atomic sizes, which involve submicroscopic scales, is difficult for students to imagine. When we say that the radius of one atom is twice that of another, students usually forget that according to the formula (4/3) x π x r^3 their volume ratio is 8. This can be analogized with two balls having this relation in their radius.

The use of analogies in teaching is a straightforward, effective, challenging and enjoyable activity, but the teacher must choose analogies which are appropriate to the audience and are better understandable.

References:

[1] D.J. Olney, *J. Chem. Educ.*, 65 (1988) 696-697.
[2] Z.R.,Dagher, *Science Education*, 79(1995a) 295-312.

Invited lecture

NMR methodology developments in the analysis of complex mixtures in natural products and food chemistry: From metabolomics to in-cell NMR

I.P. Gerothanassis

Section of Organic Chemistry and Biochemistry, Department of Chemistry, University of Ioannina, Ioannina, Greece

E-mail: igeroth@uoi.gr

IL04

An overview of recent developments of NMR spectroscopy in the analysis of complex metabolite mixtures of natural products and food chemistry will be provided with emphasis:

a. In sensitivity with the use of selective suppression of the major NMR resonances [1].
b. In resolution of (i) ^{1}H NMR resonances with emphasis on the aldehyde CH and phenol hydroxyl proton in the region of 8 to 15 ppm [2]; (ii) 2D ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC) and 2D ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC) spectroscopy [2]; (iii) diffusion-ordered spectroscopy (DOSY) [3] and (iv) selective 1D-TOCSY experiments [4]
c. In both sensitivity and resolution with the use of hyphenated LC-solid phase extraction (SPE)-NMR techniques [5].
d. In saturation transfer difference (STD), TR-NOESY and in-cell NMR experiments.
e. On data mining.

A critical overview of selected applications will be provided including: (i) metabolomic analysis of extracts of oregano species and lipid fractions of dairy products [1], [2], [4], [6] without isolation or derivatization steps [6], (ii) 'in situ' direct monitoring of dynamic changes of metabolites as a function of solvent and temperature [7], (iii) rapid 'in situ' analysis of enzymatic reaction products [8] and (iv) in-cell NMR in decoding the apoptotic activity of flavonoids from natural products and food stuff with the Bcl-2 family of proteins [9].

This research has been co-financed by the the Cyprus Research Promotion Foundation.

References

[1] C.G. Tsiafoulis et.al. *Anal. Chim. Acta*, *821*, 62-71 (2014).
[2] P. Charisiadis, et.al. *Chem. Commun*., 46 (2010) 3589-3591; A. Nerantzaki, et.al. *Anal. Chim. Acta*, 688 (2011) 54-60; P. Charisiadis, et.al. *J. Nat. Prod*., 74 (2011) 2462-2466; P. Charisiadis et.al. *J. Agric. Food Chem*., 60 (2012) 4508-4513; V. Kontogianni et.al., *Org. Biomol. Chem*., 11 (2013) 1013-1025.
[3] A. Primikyri et.al. *Tetrahedron*, 68 (2012) 6887-6891.
[4] Manuscript submitted.
[5] V. Goulas, et al. *LWT-Food Science and Technology*, 46 (2012) 104-109.
[6] P. Charisiadis et al. *Molecules*, *19*, 13643-13682 (2014).
[7] P. Charisiadis et al. *Magn. Reson. Chem.*, in press. DOI:10.1002/mrc.4/29.
[8] E. Kyriakou et.al. *Org. Biomol. Chem.*, 10 (2012) 1739-1742; manuscript in preparation.
[9] A. Primikyri et al. *ACS Chem. Biol.* (2014), in press.

Monday 21 September 2015

Royal Cruise Hall-A

Chair: D. Knopp, I. Gerothanassis

Food Analysis 1

Invited lecture

Analytical approaches to evaluate structure – property relations of soluble cereal fibers and their impact to food product quality and physiological functionality

C.G. Biliaderis

Dept. Food Science and Technology, Aristotle University of Thessaloniki,
541 24 Thessaloniki, Greece

E-mail: biliader@agro.auth.gr

Epidemiological and clinical studies continue to link the consumption of cereal grain products, specifically cereal fibers, with reduction of risk and/or better management of several chronic inflammatory conditions (cardiovascular disease, diabetes, obesity and certain types of cancer). Mixed linkage β-1→3, 1→4 D-glucans, for example, from non-processed or minimally processed oat and barley grains, are among the very few food components that have obtained a positive statement for approved health claim status by FDA and recently by EFSA (glycemic response and cholesterol-related), with recommendations for daily intake of at least 3 g of β-glucan in one or more servings. However, until now, the physiological mechanisms behind the health benefits are not fully understood, although extractability-solubility, viscosity, and molecular weight seem to play a role, particularly when considering composite food matrices. Moreover, the use of cereal fibers in the form of concentrates or isolates as thickening or bulking agents in formulated products, to modify texture and stability of the product in addition to conferring specific health benefits, remains a true challenge to the food technologist from a processing-formulation and sensorial perspective.

The molecular features (fine structure and molecular size) of cereal fibers (mostly β-glucans and arabinoxylans) can vary depending on the source (genotype) and plant tissue as well as on environmental and processing conditions employed during their isolation and product manufacturing. It is thus essential to explore the molecular basis of the physicochemical and physiological functionality of these materials in order to optimize their function - physiological properties as well as the quality of food products formulated with such sources of dietary fiber (DF). In this respect, an integrated analytical approach must be taken, involving various techniques for molecular size and structure elucidation (^{1}H and ^{13}C-NMR spectroscopy, enzymic methods in conjunction with several chromatographic methods, etc.) and determination of the physicochemical properties of the polymeric components of DF (thermal analysis, rheometry etc.), in order to establish a better understanding of the structure-function relations of these components; in this way, a full exploitation of their applications as functional hydrocolloids in food formulations can be sought.

The objective of this paper is to address some of the analytical approaches used to obtain information on structure - function relationships of soluble cereal fibers in the context of their technological (food quality and product stability related issues) and physiological functionality in model systems and in real food products.

A high-throughput SNP-genotyping method based on fluorescent microspheres for olive oil varietal identification

D.P. Kalogianni[1], C. Bazakos[2,3], L.M. Boutsika[1], M. Ben Targem[2], Th.K. Christopoulos[1,4], P. Kalaitzis[2] and P.C. Ioannou[5]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504.
[2]Department of Horticultural Genetics & Biotechnology, Mediterranean Agronomic Institute, Chania, Greece 73100.
[3]Present address: INRA, UMR 1318, Institut Jean-Pierre Bourgin, RD10, F-78000, Versailles, France.
[4]Institute of Chemical Engineering and High Temperature Processes, Foundation of Research and Technology Hellas, GR-26504 Patras, Greece
[5]Department of Chemistry, University of Athens, Athens, Greece 15771.

E-mail: tchrist@upatras.gr

MO01

The determination of the olive cultivar utilized to produce an olive oil sample is of primary importance in order to enhance the competitiveness of the product and protect both the consumer and the producer by preventing fraudulent practices. Single nucleotide polymorphisms (SNPs) are recognized as excellent DNA markers for authenticity tests. In this work, we report the first multiplex SNP genotyping assay for olive oil cultivar identification that is performed on a suspension of spectrally encoded microspheres in a high-throughput and cost-effective format. Different sets of microspheres that are stained with various amounts of two spectrally distinct fluorophores, providing up to 100 different sets, which in turn permit the rapid simultaneous genotyping of up to 50 SNPs, have been used. Allele discrimination was accomplished through primer-extension reaction. The products were biotinylated, captured from a suspension of microspheres and detected by a streptavidin-phycoerythrin conjugate. The microspheres were then analyzed, within seconds, by a flow-cytometer. Each microsphere 'fluorescence signature' corresponds to a specific allele whereas the positive signal of the phycoerythrin reporter denotes the presence of this allele in the sample. As a model, a panel of three SNPs (6 alleles) was chosen for the identification of five olive cultivars (Adramytini, Chondrolia Chalkidikis, Kalamon, Koroneiki and Valanolia) that are common in Greece. The method gave accurate and precise results. For each cultivar, DNA isolated from leaf samples gave identical genotypes with DNA isolated from olive oil [1].

References

[1] D. Kalogianni, C. Bazakos, L. Boutsika, M. Targem, T. Christopoulos, P. Kalaitzis and P. Ioannou, *J Agric Food Chem.*, 63 (2015) 3121-3128.

Perspectives and opportunities in plant and food science research of synchrotron microscopy and spectroscopy techniques

D. Eichert

Elettra – Sincrotrone Trieste, S.S. 14 Area Science Park, 34149 Basovizza, Trieste, Italy

E-mail: diane.eichert@elettra.eu

MO02

The research challenges and questions faced in plant or food science occur over multiple spatial and temporal scales and levels, involving complex reactions at physiological, physical and chemical interfaces between abiotic and biotic components of the soil and atmosphere.
Pushing the knowledge limits further undoubtedly involves the use of advanced, in situ technologies in combination with interdisciplinary research, and linking macroscopic measurements with micro-scale investigations. The necessity of molecular, environmental, and interfacial characterization within plant tissues and sub-tissues at sub-cellular level is becoming increasingly important, with an examination on localized and specific areas. Realistically, as biological based materials are highly heterogeneous and complex by nature, not a single technique can answer all the questions. With the advent of state-of-the-art synchrotron imaging/micro-spectroscopy based techniques, the simultaneous elucidation of physiological mechanisms and structural biochemistry at micro-scales can be undertaken [1]. The challenge resides in sample preparation, sample environment for characterization and on the successive applications of the techniques. Indeed, resolving the distribution, status, competition and concentration of elements and molecules within the different morphological structures of a specific physiological tissue is essential for understanding the mechanisms involved in their regulation, allocation, absorption, transport, accumulation, functionality and bioavailability.
To fulfill that purpose, multifaceted and interdisciplinary synchrotron radiation (SR) based imaging techniques were successfully correlated to provide highly sensitive spatially resolved chemical analysis. In particular, common wheat seeds [2] and hyperaccumulating *Thlaspi Praecox* leaves [3] and seeds were probed via SR-FTIR, to reveal the type, distribution and relative amount of functional and molecular groups, SR-X-ray spectro-microscopy, to obtain high resolution imaging of the morphology of the specimen by many contrast mechanisms (transmission, differential phase contrast, brightfield and fluorescence), and SR-X-ray computed microtomography, to elucidate non-invasively the 3D structural arrangements of organs and tissues. These combined studies are leading to significant new insights on plant morphology, structural biochemistry, reactivity and physiological relevance.

References

[1] D. Eichert, L. Gregoratti, B. Kaulich, A. Marcello, P. Melpignano, L. Quaroni and M. Kiskinova, *Analytical and Bioanalytical Chemistry*, 389 (2007) 1121-1132.
[2] M. Regvar, D. Eichert, B. Kaulich, A. Gianoncelli, P. Pongrac, K. Vogel-Mikus and I. Kreft, *Journal of Experimental Botany*, 62 (2011) 3929-3939.
[3] M. Regvar, D. Eichert, B. Kaulich, A. Gianoncelli, P. Pongrac and K. Vogel-Mikus, *Plant Soil*, 373 (2013) 157-171.

DNA-based meat authenticity testing by a multianalyte fluorometric method

V.M. Myridaki[1], I.K. Kyriakou[1], D.P. Kalogianni[1], P.C. Ioannou[2] and Th.K. Christopoulos[1,3]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504.
[2]Department of Chemistry, University of Athens, Athens, Greece 15771.
[3]Foundation for Research and Technology Hellas/Institute for Chemical Engineering Sciences, Patras, Greece 26504

E-mail: tchrist@upatras.gr

MO03

Authentication of meat products is of great importance for the protection of consumers from fraud. Consequently, there is an increasing demand to develop improved analytical methods for the accurate identification of the meat species in food products and the detection of adulterants. To this end, we have developed a DNA-based assay that enables simultaneous detection of beef, pork, sheep, horse, chicken and turkey meat. The advantages of the proposed multianalyte assay include high sample-throughput, cost reduction and lower sample and reagents consumption. DNA isolated from the food sample was subjected to polymerase chain reaction (PCR), in which species–specific DNA sequences were amplified exponentially using biotinylated primers. The sizes of the amplified fragments were 96, 144, 88, 107, 72 and 223 bp for beef, pork, sheep, horse, chicken and turkey meat, respectively. The PCR products were thermally denatured and detected by a multianalyte hybridization assay performed on spectrally encoded fluorescent microspheres (5000 microspheres for each species of meat). The microspheres' surface was functionalized by covalent attachment of species-specific oligonucleotide probes. Phycoerythrin-conjugated streptavidin was employed as a reporter. Following hybridization, the microspheres were interrogated individually by flow-cytometry. The flow-cytometric detection step was completed in less than 1 min. During this process, each microsphere was irradiated by 2 lasers simultaneously (635 nm and 532 nm). The 635 nm beam revealed the species of meat (based on the specific probe that was attached to the microsphere) whereas the 532 nm beam excited the bound phycoerythrin whose fluorescence increased with the amount of species-specific DNA sequence. The proposed method can be easily expanded to the multianalyte detection of more species, since there are 100 spectrally distinct sets of commercially available microspheres.

Antioxidant capacity of the extracts from heather (*Calluna vulgaris* L. Hull) flowers

K. Pyrzyńska[1], P. Dróżdż[2]

[1]Laboratory for Flow Analysis and Chromatography, Department of Chemistry, University of Warsaw, Poland
[2]Laboratory of Environmental Chemistry, Forest Research Institute, Sękocin, Poland

E-mail: kryspyrz@chem.uw.edu.pl, p.drozdz@ibles.waw.pl

MO04

Calluna vulgaris L. Hull (heather) can be found in most parts of Europe. Flowers of heather are rich source of polyphenolic compounds such as flavonoids, phenolic acids, procyanidins, sterols and triterpenes [1]. The extracts from plant material are a part of traditional folk medicine for treating urinary tract disturbances and inflammatory related disorders [2]. Moreover, flowers of heather are components in herbal mixtures used in some cosmetic products.

The aim of this study was to investigate the content of some polyphenols and antioxidant capacityfound in extracts of the aerial parts of *Calluna vulgaris* (L.) Hull. Samples were collected in Forest District Wyszków in Poland in September 2014. Water, ethanol and its mixture as well as ethyl acetate were used for extraction. The influence of extraction temperature was also studied. Antioxidant capacity of the prepared extracts was screened by several spectrophotometric methods: Folin-Ciocalteu (so-called total phenolic content), cupric ion reducing antioxidant capacity (CUPRAC), $DPPH^{\bullet}$ and aluminium chloride method (so-called total flavonoids content). The content of some polyphenols was determined by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS).Gradient elution was used: 8 mM formic acid (pH 2,8) and acetonitrile. Compounds were identified by retention time, MS and MS^2 spectrum for standard references.

Flavonoids: quercetin, rutin, quercetrin, luteolin, apigenin, catechin, epicatechin and phenolic acids such as ferullic, gallic and chlorogenic acid were determined in the extracts from heather flowers. Phytochemistry of heather extracts and its antioxidant capacity strongly depend on the used extractant. The highest content of polyphenols was found in 60% ethanol, the lowest, especially for quercetin and rutin glycosides, was obtained when water was used.

References

[1]. M. Monschein,J. I. Nira, O. Kunert, F. Bucar, *Phytochemistry Review*, 9 (2010) 205-215.
[2]. L. Hooper, A. Cassidy, *Journal Science of Food and Agriculture*, 86 (2006) 1805-1813.

Invited lecture

Luminescent methods for the evaluation of antioxidant activity of olive oil and other natural products

A.C. Calokerinos[1] and R. Apak[2]

[1] Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece
[2] Department of Chemistry, İstanbul University, Faculty of Engineering, Avcılar, 34320 İstanbul, Turkey

IL06

Luminescent methods are based on the excitation of molecules either by absorption of light (photoluminescence, fluorescence) or by a chemical reaction (chemiluminescence: CL) and are characterized by simplicity, sensitivity, low limits of detection and relatively low cost instrumentation. These advantages enabled the utilization of luminescence spectroscopy in numerous applications of analytical chemistry including food and edible oil analysis. However, the majority of luminescent methods in oil analysis concern oil extracts and not untreated oils due to the fact that the sample is not miscible with water. Nevertheless, any treatment of oil prior to analysis, such as extraction, changes the chemical composition of the tested sample which might lead to erroneous results. Hence, direct application of analytical methods to oil without any pretreatment except dilution would be preferable.
The CL reactions of luminol and lucigenin have been widely exploited for the determination of hydroperoxides in untreated oils using microemulsions and homogeneous solutions, naturally bringing certain problems associated with sample exposure to reagents, phase behavior, and possible interference from compounds present in oil. Additionally, two widely applied spectrophotometric methods, the Fe(III)-phenanthroline and the CUPRAC assays, have been adapted to untreated oils *via* selection of mixture of solvents (ethanol–butanol in 3:1 v/v ratio), and optimization of the reaction conditions (reagents concentration and reaction time).
This presentation describes the application of luminescent methods in the analysis of edible oils without any pretreatment such as extraction prior to analysis. Emphasis has been given to applications of chemiluminescence and fluorescence assays for determining quality parameters of edible oils, such as oxidative stability, antioxidant activity, and lipid hydroperoxides content, as well as classification or adulteration of vegetable oils.

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund.

European Union
European Social Fund
OPERATIONAL PROGRAMME EDUCATION AND LIFELONG LEARNING
investing in knowledge society
MINISTRY OF EDUCATION & RELIGIOUS AFFAIRS
MANAGING AUTHORITY
NSRF 2007-2013
programme for development
EUROPEAN SOCIAL FUND
Co- financed by Greece and the European Union

Monday 21 September 2015

Royal Cruise Hall-D

Chair: E. Rosenberg, L. Farmakis

Food Analysis 2

New strategies of microbiological monitoring in food plants and water dispensers

L. Bolelli[1], E. Ferri[1], G. Lasi[2], S. Gozzi[3], R. Moretti[4] and S. Girotti[1]

[1]Department of Pharmacy and Biotechnology, University of Bologna,
Via San Donato 15, 40127 Bologna, Italy.
[2]Granarolo SpA., Via Cadriano 27/2, 40127 Bologna, Italy.
[3]CAMST Scrl, Via Tosarelli 318, 40050 Villanova di Castenaso, Bologna, Italy.
[4]Culligan Italiana SpA, Via Gandolfi, 6, 40057 Cadriano di Granarolo Emilia, Bologna, Italy

E-mail: stefano.girotti@unibo.it

MO05

An effective monitoring of microbial contaminations on working surfaces or plant components is of fundamental importance in activities dealing with food, water included manipulation and distribution. The microbiological tests can supply information after 1-2 days, the rapid luminescent ATP assay after about 5 minutes and on site when performed on portable instrument [1]. The timely identification of unwanted contamination is necessary to ensure quality and safety of foods.
The aim of this work was to assess the hygiene conditions of: a dairy industry "High Quality" production line, of its work canteen, of dispensed water and of components of different water coolers model. The quantification of the bacterial content has been based on the rapid luminescent ATP assay, compared with the classical plate counts. To assess the presence of E. coli, the total coliforms amount, Enterococci and P. aeruginosa were employed colorimetric-fluorescent kits. The samples have been obtained by swabbing work surfaces (100 cm^2) or 2 cm of the cooler tubes, or sampling the dispensed water.
The microbiological and the luminescent ATP assay data resulted in all tests in good agreement allowing stating the reliability of the rapid luminescent test. All samples taken at the High Quality dairy production line were under the threshold values, while a critical situation was found at the worker's canteen. A bench was continuously re-contaminated from a too close kitchen sink. Water coolers components and inner surfaces revealed bacterial contaminations and biofilm, not completely removed by the chemical sanitization procedures. ATP assay resulted very useful in quickly found out the correct sanitization protocols and the alternative, effective solutions (addition of UV lamps or medical filters) ensuring the constant quality of dispensed water.
Conclusion
The rapid ATP test was confirmed as a rapid and reliable tool to assess hygiene conditions and allowing easily to evaluate and compare different sanitization treatments. The assay is simple to perform and any unsatisfying situation can be resolved straight after.

References

[1] P. Caputo, E.N. Ferri, S. Girotti, S. Gozzi and P. Saracino, *Czech Journal of Food Sciences*, 29 (2011) 382–390.

Development of microemulsion electrokinetic chromatography method for the analysis of illegal fat-soluble foodstuff dyes

K. Petrů, J. Bradová, L. Pincová and M. Polášek

Charles University of Prague, Faculty of Pharmacy in Hradec Králové, Heyrovského 1203, CZ 500 05 Hradec Králové, Czech Republic

E-mail: polasek@faf.cuni.cz

MO06

A microemulsion electrokinetic chromatography (MEEKC) method was developed and proposed for the determination of fat-soluble dyes (Sudan I, Sudan II, Sudan III, Sudan Red 7B, Sudan Orange G, and Methyl Red) illegally used in foodstuffs. The effect of surfactant, co-surfactant, organic modifier and oil as well as the capillary length were examined in order to optimize the separation. Final background electrolyte (solution of the microemulsion) for MEEKC was composed of 30 mM phosphate buffer (pH 7.5), 1.2% (w/v) sodium dodecylsufate, 1.2% (v/v) of n-hexane, 15% (v/v) of butan-1-ol, and 20% (v/v) of acetonitrile. A baseline separation of these six dyes was achieved within 11 min by using fused-silica capillary with 75 µm i.d. and effective length 36.5 cm. The applied voltage was 20 kV and temperature 25°C was maintained. The VIS detection wavelengths were 500 and 430 nm. The repeatability of the migration times and peak areas were characterized by RSD values ranging from 0.3 to 0.8% and 1.7 – 3.0% (n = 6), respectively. The calibration curves were linear for all analytes ($r^2 \geq 0.9985$) and the limits of detection ranged from 0.16 µg/ml (for Methyl Red) to 1.27 µg/ml (for Sudan Red 7B). The method devised is suitable for the analysis of suspected foodstuffs after appropriate sample pretreatment to eliminate matrix effects and to achieve sample pre-concentration.

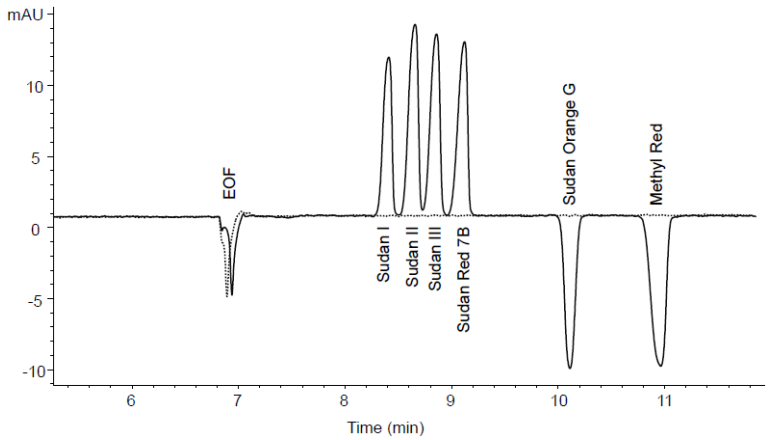


Fig.1: *MEEKC separation of standard mixture of illegal foodstuff dyes under optimum conditions (dotted line: blank sample)*

Acknowledgements: *Financial support from SVV 260 184 and the European Social Fund and the State budget of the Czech Republic, Project no. CZ.1.07/2.3.00/30.0061are gratefully acknowledged.*

Characterization of multifunctional *Haematococcus pluvialis* extracts and their application in beverage products

S. Papadaki, V. M. Christopoulou, C. Drosou, K. Tataraki, K. Kyriakopoulou, A. Pappa and M. Krokida

School of Chemical Engineering, National Technical University of Athens, Zografou Campus, GR-15700 Athens, Greece

E-mail: spcheng@central.ntua.gr

MO07

The consumption of soft drinks and beverages is a daily habit of a large part of the population, particularly of children and adolescents. The limited shelf-life of the fresh beverages imposes the use of enhancers. The majority of beverages enhancers are synthetic and their excessive consumption has been accused for several health disorders and chronic diseases [1]. The new European regulation for food additives (1129/2011) intends to restrict or decrease the use of numerous synthetic enhancers and to impose their replacement with natural ingredients. In this study, multifunctional extracts from *Haematococcus pluvialis* microalga have been suggested as beverage enhancers. *H. pluvialis* is a green unicellular Chlorophyta alga able to accumulate high levels of astaxanthin (up to 2% of its dry weight). Astaxanthin-rich Haematococcus has already been marketed as a dietary supplement for human consumption [2]. The health benefit of this product is mainly due to its strong antioxidant activity, which is 100 times more than a-tocopherol. Moreover, astaxanthin has an antioxidant action up to 500 times that of vitamin E and is the most stable antioxidant and never turns into a pro-oxidant. The range of shades from astaxanthin includes red as well as orange. Therefore, it can replace synthetic ones such as Tartrazine, Sunset Yellow etc. Moreover, the significant antioxidant activity that astaxanthin presents can sufficiently compete and replace synthetic antioxidants such as BHA, BHT [3].

In the frames of this study, extracts obtained using a green and energy efficient extraction technique, the ultrasound assisted extraction, and green solvents such as Medium Chain Triglycerides and essential oils as well as conventional ones such as acetone were characterized through analytical methods in order to be evaluated as appropriate beverage enhancers. Specifically, the pigments content (total carotenoids, b-carotene, chlorophylls, asxtaxanthin) [4, 5] was measured spectrophotometrically. Moreover, the carotenoids profile was evaluated using HPLC-DAD technique [6]. Finally, the Total Lipids profile was studied using GC chromatography [7].

References

[1] F. Gultekin and D.K. Doguc, *Clin. Rev. Allergy Immunol,.* 45 (2013) 6–29.
[2] N. Drago, V. Bercea, A. Bica, B. Drug, and A. Nicoar, (2010).
[3] B.K Ishida and M.H. Chapman, *J. Agric. Food Chem.,* 57(2009) 1051–1059.
[4] S.W. Jeffrey and G.F. Humphrey, *Biochem. Physiol. Pflanz* ,167(1975) 191–194.
[5] A. Ben-Amotz and *M.* Avron, *Plant Physiol,.* 72 (1983) 593–597.
[6] I.F. Strati and V. Oreopoulou, *Food Chem.,* 129 (2011) 747–752.
[7] G. Lepage and C.C. Roy, *J. Lipid Res.,* 27(1986) 114–120.

Determination of physicochemical parameters as a function of time for physically adsorbed or chemisorbed aroma compounds on starch granules from different origin by inverse gas chromatography

K.A. Eftaxopoulou[1,2], L. Farmakis[1], A. Koliadima[2], G. Karaiskakis[2], J. Kapolos[1]

[1] Food Technology Department, Technological and Educational Institute of Peloponnese, 24100 Kalamata, Greece
[2] Chemistry Department, University of Patras, 26504 Patras, Greece

E-mail: akoliadima@upatras.gr

MO08

The main factor influencing the fixation of aroma compounds on food is the nature of the solid. These interactions are dominated by three mechanisms: a) the distribution of aroma compounds between different phases of food, b) the diffusion of aroma compounds through the bulk of food and c) the linking of aroma compounds with food components. Starch is one of the food component which have the ability to interact with aroma compounds in two different ways: a) by simple absorption and b) by physical encapsulation in the bulk. The mechanism of this interaction depends on the type of compound the morphological and energetic properties of the surface and of the composition of the starch molecules. Surface characterization of starch granules is of great importance in order to investigate this interaction.

Physicochemical parameters for adsorption of aroma compounds on starch granules are measured as a function of time. Local isotherms, θ, against adsorption energy, ε, fractional changes of adsorption sites $f(\varepsilon) / c^{*}_{max}$ against ε, and θ against $f(\varepsilon) / c^{*}_{max}$ were calculated. The method uses only chromatographic experimental data obtained by the inverse gas chromatography technique known as reversed-flow gas chromatography. It was applied to study the adsorption of dl-limonene and diacetyl onto particles of starch from wheat, rice, potato and corn at different temperatures. Also from the results the time separation of experimental surface energy together with the time-independent rate constants for adsorption and desorption of aroma compounds on starch granules is described.

Acknowledgment

This research has been co-financed by the European Union (European Social Fund–ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF)-Research Funding Program: ARCHIMEDES III. Investing in knowledge society through the European Social Fund

Monday 21 September 2015

Royal Cruise Hall-A

Chair: C. Biliaderis, T. Varzakas

Food Analysis 3

Invited lecture

Bioanalytical determination of mycotoxins in food samples – an overview of current concepts and trends

D. Knopp and R. Niessner

Institute of Hydrochemistry and Chair for Analytical Chemistry, Technische Universität München, Marchioninistrasse 17, 81377 München, Germany

E-mail: Dietmar.Knopp@ch.tum.de

Food safety is increasingly becoming an important health issue, as food-borne diseases present a widespread and growing public health issue in both developed and developing countries. Modern analytical chemistry is gaining in importance in food quality and safety monitoring. There are continuous ongoing efforts to develop rapid, low-cost, simple and reliable tests for first-level screening of food contaminants, which could also be automated, or carried out on-site. Amongst currently emerging techniques, significant attention has been given to bio-analytics, and especially to the development of new nucleic acid-based and immunological techniques.
This presentation will cover the techniques used nowadays to produce highly specific and affine antibodies against mycotoxins. Among others, ***polyclonal (pAb) and monoclonal (mAb) antibodies*** remain the dominant binders used for many applications. Further, new ***recombinant antibody (rAb)*** techniques now provide exciting possibilities allowing, for example, more efficient manipulation of antibody paratopes. In addition, the expression and purification of recombinant antibodies (so-called ***plantibodies***) produced in plants is emerging as an affordable alternative to using more costly mammalian bioreactors since plants are capable of producing mammalian proteins at high concentrations. Moreover, artificial nucleic acid ligands – the ***aptamers*** – are gaining increasing interest as new recognition reagents since their first discovery in 1990. During the last decades, several advantages of aptamers, compared to natural receptors such as antibodies, have attracted researchers to develop aptamer-based assays. ***Immunoassays*** come in adverse range of formats, and ***ELISAs*** are currently the most popular. However, as demand grows for even shorter analysis time and more user-friendly assays, other formats like ***lateral-flow devices*** and ***flow-through tests*** are also being explored. A major disadvantage of many current immunoassays (compared with separation techniques) is that they commonly have limited multianalyte capabilities. This is being addressed using ***multiplexed assays*** with immune biochips (***microarrays***) or encoded microspheres (***bead-based microfluidic assays***). Despite historic achievements in the field of label-free assays (both optical and non-optical), labeling techniques will continue to play a leading role in bioanalytics. In addition to enzyme, and fluorescence labels, improved performance immunoassays using artificial particulate markers (organic or inorganic) are of increasing interest since they may permit, for example, reduced detection limits and signal amplification. Further research is also increasingly looking to develop innovative and powerful novel ***bio-functionalized nanometer-sized particles***.

Migration of specific metals in canned foods before and after opening. Validation of a new quality indicator for opened cans

G. Petropoulos[1], I. Passias[2], N. Thomaidis[2] and C. Proestos[1]

[1]National and Kapodistrian University of Athens, Department of Chemistry, Food Chemistry Laboratory, Panepistimiopolis Zografou, 15771 Athens, Greece
[2]National and Kapodistrian University of Athens, Department of Chemistry, Laboratory of Analytical Chemistry, Panepistimiopolis Zografou, 15771 Athens, Greece

E-mail: harpro@chem.uoa.gr

MO09

A method for the simultaneous determination of Cd-Pb, As-Cu, Cr-Ni and Fe-Mn in canned food samples by Electrothermal Atomic Absorption Spectrometry was developed and validated. The validation procedure was conducted according to the terms of the European regulation for the official control of contaminants in foods. The validated methods were applied for the determination of these metals and metalloids in more than 20 different samples. Furthermore, a new quality indicator was evaluated in order to provide information about canned foods quality and the appropriate storage time of opened canned food samples. The case of tomato paste will be presented where a migration test was accomplished based on the calculation of mass balance and the comparison of the elemental content in canned tomato paste samples and in aseptic paper pack.

References

[1] I.N. Pasias, V. Papageorgiou, N.S. Thomaidis and Ch. Proestos, *Food Anal. Methods*, 5 (2012) 835–840.
[2] Ch. Proestos, I.N. Pasias, V. Papageorgiou, K. Barmperis and N.S. Thomaidis. Tadahisa Higashide (Ed.), Tomatoes: Cultivation, Varieties and Nutrition, Nova Science Publishers Inc., New York (2013), pp. 275–288 (Chapter 16), ISBN: 978-1-62417-915-0.

Raman spectroscopy for the authentication of Greek extra virgin olive oil and adulteration with sunflower oil

A. Philippidis and M. Velegrakis

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1385, GR-711 10 Heraklion, Crete, Greece

E-mail: filagg@iesl.forth.gr

MO10

Extra virgin olive oil (evoo) is a natural juice, which is superior compare to other oils. It is appropriate to human's nutrition because of the moderate levels of unsaturated fatty acids and the rich presence of vitamin E. Compared to common vegetable oils, the cost of the evoo is higher. As a result, it is common habit, the extra virgin olive oil adulteration with seed oils or low-quality olive oils. [1] The last years for authenticity and adulteration detection of evoo different analytical techniques, that offer qualitative and quantitative information, were used. Vibration spectroscopy as Raman technique was find application in determination of olive oil adulteration.[2-3]

Raman spectroscopy is a fast, simple analytical technique that is non-invasive and does not require sample pre-treatment. The specific vibrational spectroscopy is appropriate in discrimination of chemically similar samples (molecules) as the different types of oils. In this work we use a mobile Raman spectrometer with a laser source at 786 nm (near-infrared). The mobility of the system helps to on-site analysis of oils and the in situ monitoring of olive oil adulteration. Raman spectroscopy was employed to authentication of Greek extra virgin olive oil and its adulteration with sunflower oil.

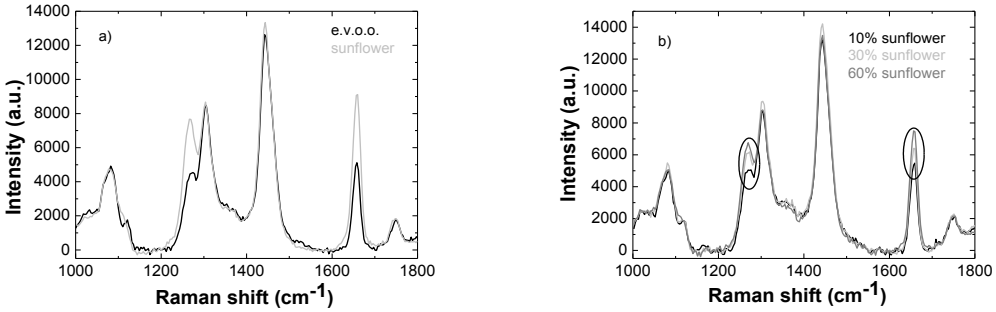


Fig. 1: Raman spectra (after baseline correction) of a) e.v.o.o. and sunflower oil and b) binary mixtures of them.

References

[1] D. Boskou, *AOCS Press*, Chapter 8 (1996) 121-133.
[2] E. C. L.-Diez, G. Bianchi and R. Goodacre, *J. Agric. Food Chem.*, 51 (2003) 6145-6150.
[3] M.-Q. Zou, X.-F. Zhang, X.-H. Qi, H.-L. Ma, Y. Dong, C.-W. Liu, X. Guo and H. Wang, *J. Agric. Food Chem.*, 57 (2009) 6001-6006.

Fatty Acids composition of Greek PDO and Traditional Cheeses, a statistical analysis on their profile acquired by a GC/FID method

G. Karanikolopoulos, L. Kioupis, K. Papadopoulou and I. Mastrantoni

General Chemical State Laboratory, Chemical Division of Piraeus and Aegean, 32 Etolikou Str., 185 10 Piraeus

E-mail: piraeus_aegean@gcsl.gr

MO11

The fatty acid (FA) composition of dairy products has been widely investigated in recent years towards gaining additional insight on their effect on human health. It has been established that many saturated (i.e. C12:0, C14:0 and C16:0) and trans fatty acid increase the risk of coronary heart disease. On the other hand, some unsaturated fatty acids have been pointed as critical compounds for protecting against cardiovascular diseases as well as inhibiting degenerating cell proliferation [1,2].

In the present study, the fatty acid composition of several cheeses marketed in Greece either as PDO or traditional products was studied. The work aimed at establishing the average Fatty Acid Profile of popular Greek PDO and other traditional Greek cheeses. The presence of a unique fatty acid profile "footprint" for each category of PDO cheeses was also examined. For that purpose, different PDO and Traditional cheeses obtained from Hellenic market were analyzed in the past five years on the basis of adulteration detection and authentication issues. Differences were observed in fatty acid composition between cheeses which can be attributed to the origin of milk (cow's as opposed to sheep's or goat's milk) and/or animals' diet (including forage type) and physiology [3].

Determination of fatty acid composition in milk fat was based on ISO 15885/IDF 184 and ISO 15884/IDF 182. The method, which was fully validated in our laboratory, is based on the conversion of milk fat triglycerides to Fatty Acid Methyl Esters (FAMEs) by transesterification. The resulting FAMEs were separated by capillary gas-liquid chromatography coupled with a flame ionization detector (GC/FID) and the chromatograms were evaluated.

Furthermore, statistical analysis revealed significant differences in some fatty acids content between cheeses made from cow's milk and sheep's/goat's milk. These findings can provide a useful tool, along with findings from other analytical sources, for the verification of the authenticity for traditional products, as well as the detection of adulteration in those products.

Finally, data on nutritional facts such as Saturated/non-saturated ratio, Atherogenicity and Thrombogenicity indexes for the Greek cheeses are presented and discussed.

References

[1] K.J. Shingfield, Y. Chilliard , V. Toivonen, P. Kairenius, D.I.Givens, Trans Fatty Acids and Bioactive Lipids in Ruminant Milk, in: Bösze Z. (Ed.), Advances in Experimental Medicine and Biology — Bioactive Components of Milk, Springer, New York, USA, 2008, 3–65.

[2] C.M.Williams, *Ann. Zootech.*, 49 (2000)165–180.

[3] M.Addis, A.Cabiddu, G.Pinna, M.Decandia, G.Piredda, A.Pirisi and G.Molle, *J. Dairy Sci.*, 88 (2005) 3443–3454.

The application of FT-IR technique in characterizing food microencapsulation systems

C. Chranioti[1], A. Karamberi[2], L.-A. Tsakanika[2] and C. Tzia[1]

[1]Laboratory of Food Chemistry and Technology, School of Chemical Engineering, National Technical University of Athens
[2] Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens

E-mail: tzia@chemeng.gr

MO12

FT-IR techique, providing information about chemical bonds and molecular structure changes of materials, can be used in characterizing food microencapsulation systems. In particular, it can be applied in order first to verify the presence of a substance (core material) into the microencapsulation system and second to provide further evidence of the way the substance is entrapped into the matrix; chemical, intramolecular or intermolecular interaction [1]. Moreover, it can be applied to prove the formation of complexes between core substance and microencapsulating agent in solid state [2].

In the present work the entrapment of fennel oleoresin (FO) in different biopolymer matrices was studied. The biopolymers used including modified starch (MS), maltodextrin (MD), chitosan (CH) and gum arabic (GA) in pure, binary and ternary formulations. The applied entrapment systems involved freeze-drying, spray-drying and complex coacervation technique.

Based on the obtained results, the FT-IR spectrum of fennel oleoresin was dominated by the bands at 2925 cm^{-1}, 2854 cm^{-1} and 1747 cm^{-1}, on the basis of which the discrimination was conducted. The appearance of the above characteristic bands in the spectra of the studied samples verifies the presence of FO in the freeze and sprayed dried products. Moreover, the fact that no new bands or shifts of the already existing ones were observed means that no chemical reaction between FO and carrier took place. This result provides further evidence of the entrapment of FO in the agents by intermolecular interaction, since no chemical ones were detected.

In the case of complex formation, GA-CH and GA-MD-CH samples presented a very low intensity band at 1263 cm^{-1} which is attributed to the presence of carboxyl acid groups (-COOH) of gum arabic, indicating that most of the acid groups interacted electrostatically with the amine groups ($-NH_3$) of the chitosan. This result was also in consistent with the ζ-potential analysis of the samples. Therefore, FT-IR technique in combination with ζ-potential measurements can be a useful indicator of likely electrostatic interactions, providing further information regarding complex formation.

References

[1] S. Beirão-da-Costa, C. Duarte, A.I. Bourbon, A. C. Pinheiro, M. Isabel, N. Januário, A.A. Vicente, M. L. Beirão-da-Costa and I. Delgadillo, *Food Hydrocolloids*, 33 (2013) 199-206.
[2] C. Butstraena and F. Salaün, *Carbohydrate Polymers*, 99 (2014) 608- 616.

Invited lecture

Production model and international market for greek table olives

D. Calderon and P. Konstantopoulos

Kosntantopoulos S.A., Food Industry, Greece

Email: diego@konstolymp.gr, prokonstant@konstolymp.gr

IL08

The existence of the olive tree dates back to the twelfth millennium BC in Asia Minor. With the discovery of America (1492) olive farming spread beyond its Mediterranean confines. The first olive trees were carried from Seville to the West Indies and later to the American Continent. According to the Codex Standard for Table Olives "Table olives is the product prepared from the sound fruits of varieties of the cultivated olive tree (Olea europaea L.)" The olive fruit has a bitter phenolic component (oleuropein), a low sugar content (2.6-6%) and a high oil content (12-30%) depending on the time of year and the olive variety. These characteristics make it a fruit that cannot be consumed directly from the tree and it has to undergo a series of processes that differ considerably from region to region, and which also depend on variety.

Processing methods involve the transformation of bitter inedible olives into an edible foodstuff through a fermentation process, taking in consideration 3 types of olives: Green Olives, semi ripe olives and ripe olives. During fermentation, olive sugars (reduced sugars as glucose or fructose) undergo biological changes by the action of microorganisms and enzymes to produce food acids, ethanol, carbon dioxide and other metabolites. As with other types of food processing, table olives should be processed under Good Manufacturing Practices (GMP) using quality assured ingredients and procedures should be documented according to Hazard Analysis Critical Control Points (HACCP). Chemical quality criteria for table olive products involves the evaluation of the brine and olive flesh, brine analysis consider (reducing sugar levels using HPLC, Sodium Chloride levels using a salt refractometer or Volhare titration method, pH measurements using a pH meter and Total titratable acidity based on titration method with color indicator, finally table olive flesh analysis is done to evaluate moisture, oil, protein and ash content of olives.

According to the Olive Council, in the world approximately 1 million hectares of olive trees produce table olives, with a mean production during last 5 years of 2,4 millon tons of olives/year. From these around 5% are produced in Greece. In Greece 3 varieties are well known and distributed as follows: 50%Chalkidikis, 25%Conservolea and 20% Kalamata olives. There are 42 Companies that package and export table olives, and from these 10 companies sell over 5 million euros per year. During 2013, Greece exported 67 thousand tons of table olives, this volume represents 80% of the total local production, and main countries of destination are: Germany, The USA, Canada, Australia, and England.

Local market consumes around 20% of the production with higher demand for black Kalamata and Conservolea olives with 70% followed by 30% of green Chalkidiki olives. Olives in bulk presentation are preferred in the local market. Finally to comment that Greek production of table olives is increasing mainly due to the external demand, there is a tendency with farmers to cultivate green olives. Price is directly influenced by the market and production volume that change every year.

Monday 21 September 2015

Royal Cruise Hall-D

Chair: G. Karaiskakis, M. Krokida

Food Analysis 4

NMR in dairy lipid research: Improving the fatty acid profile of sheep milk by olive cake supplementation

S. Symeou[1], C. Papaemmanouil[2], C.G. Tsiafoulis[2], O. Tzamaloukas[1], D. Miltiadou[1] and I.P. Gerothanassis[2]

[1]Department of Agricultural Sciences, Biotechnology and Food Sciences, Cyprus University of Technology, P.O Box 50329, Limassol 3603, Cyprus
[2]Department of Chemistry, University of Ioannina, Ioannina GR-45 110, Greece

E-mail: sa.symeou@edu.cut.ac.cy

MO13

The aim of this study was to investigate the effect of an oil rich by-product (namely olive cake, OC) to the fat quality of sheep milk. Thirty lactating Chios ewes were allocated to the following feeding treatments: (a) no inclusion of OC (G1), (b) inclusion of 500 g/day/ewe (G2) and (c) inclusion of 1000 g /day/ewe (G3), while the other ingredients of the diet were the same. Milk samples were collected from each ewe and analysed for the content of different fatty acids (FA) and cholesterol using 1D ^{1}H-NMR spectroscopy. Briefly, the organic phase of lyophilized milk was extracted and the FA and cholesterol content identified and quantified by peak integration using appropriate calculations [1]. The effect of inclusion of OC was tested using one-way ANOVA and *Tuckey* pairwise comparisons (IBM-SPSS ver. 22). Total saturated FAs were affected (P<0.001) by OC feeding with the supplemented animals producing less saturated milk (mean values expressed in g/100g of milk fat were 78.6, 73.0 and 69.7 for G1, G2 and G3, respectively). Mono-unsaturated FAs, were increased (P<0.001) in milk from both G2 and G3 animals compared to the control group (mean values of 18.7, 24.4 and 27.3 g/100 g milk fat from G1, G2 and G3, respectively). Total unsaturated FAs were also increased (P<0.001) when OC included in the diet (mean values of 21.3, 27.0 and 30.2 g/100g fat for G1, G2 and G3, respectively). However, no differences between treatment groups were identified for linoleic and linolenic acids or cholesterol content of sheep milk. Content of conjugated linoleic acid (CLA) isomers were affected by OC supplementation (Figure 1), demonstrating an increase of CLA isomers in milk of supplemented animals. Overall, the present study using innovative NMR method showed that the inclusion of oil rich by-product in animal diets affects positively the content of milk fat in beneficial FA and the total fat unsaturation in sheep milk.

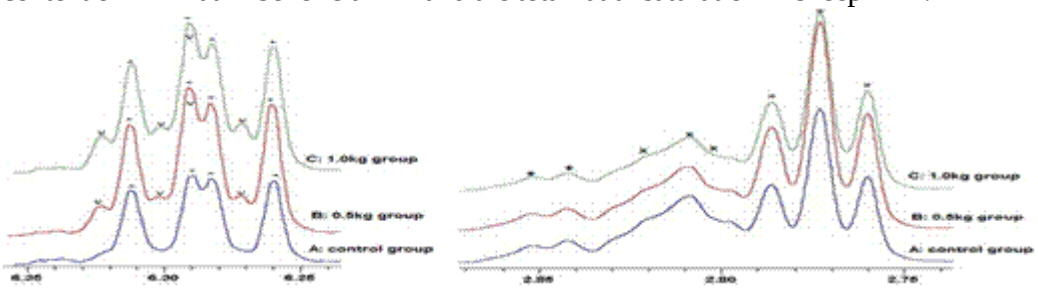


Fig. 1: *Selected regions of ^{1}H NMR spectra:* v: **H10** proton of 10-*trans*, 12-*cis* CLA at 6.27ppm, 6.29ppm, 6.30 ppm & 6.32ppm, *: **H11** proton of 9-*cis*,11-*trans* CLA & **H10** proton of 9-*trans*,11-*cis* CLA at 6.26 ppm, 6.28ppm, 6.29ppm & 6.31ppm, +: Allylic protons of polyunsaturated fatty acids (under investigation) x: Linolenic Acid (ω3 fatty acid), °: Linoleic Acid (ω6 fatty acid), A: G1, B: G2, C: G3 group

References

[1] M.A. Brescia, V. Mazzilli, A. Sgaramella, S. Ghelli, F.P. Fanizzi and A. Sacco, *Journal of the American Oil Chemists' Society*, 81 (2004) 431-436.

Virgin Olive Oil: Examining authenticity with LC-HRMS workflows

N.P. Kalogiouri and N.S. Thomaidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimioupolis Zografou, Athens, Greece

E-mail: ntho@chem.uoa.gr

MO14

Food authentication is a process by which a food is verified as complying with its label description [1]. Labelling legislation is there to ensure that food is properly described and seeks to protect the consumers as well as traders from unfair competition. Thus, food analysis is continuously requesting the development of more robust, efficient, sensitive, and cost-effective analytical methodologies to guarantee the safety, quality, and traceability of foods in compliance with legislation and consumers' demands [2]. In this respect, an analytical approach has been developed and evaluated for olive oil fingerprinting. Olive oils constituents, such as phenolic alcohols, secoiridoids derivatives, lignans, flavonoids, phenolic acids and aldehydes, were analyzed by a rapid UPLC-ESI-QToF-MS method. Generic sample extraction procedures were tested and target and suspect screening workflows were applied. Advanced chemometric tools were used to exploit the possibility of using phenolic profile as a marker for both olive oil variety and geographical origin. TOF analysis offered the possibility of searching for a large number of compounds and allowed the detection of others that were not included in the initial target list. All identified compounds could be used as markers to fingerprint and differentiate olive oils based on their aroma and taste as well as geographical origin.

References

[1] M.J. *Dennis, Analyst, 123* (1998) *151R–156R.*
[2] V. García-Cañas, C. Simó, M. Herrero, E. Ibáñez and A. Cifuentes, *Anal. Chem. 84*, 23 (2012) 10150-10159.

Proteomic-based choice and enzyme immunoassay of mammalian muscle marker for control of meat products authenticity

E.A. Zvereva[1], L.I. Kovalev[1], A.V. Ivanov[1], M.A. Kovaleva[1], A.V. Zherdev[1], S.S. Shishkin[1], A.B. Lisitsyn[2], I.M. Chernukha[2], B.B. Dzantiev[1]

[1] A.N. Bach Institute of Biochemistry, Russian Academy of Sciences, Leninsky prospect 33, 119071 Moscow, Russia
[2] The Gorbatov's All-Russian Meat Research Institute, Talalikhina street 26, 109316 Moscow, Russia

E-mail: zverevaea@yandex.ru

MO15

In modern society, a special attention is paid to control of the meat composition at every step of product manufacture. To achieve efficiency of this control, it is necessary to have reliable and high-capacity techniques that allow the identification and quantification of markers that reflect the contents of the various raw materials in the ready-made products.

Extracts from meat of different animals were compared using two-dimensional electrophoresis to identify the most efficient markers of mammalian meat. The proteins were characterized using MALDI-TOF mass spectrometry. Specific features of the main sources of mammalian meat (pork, beef) have been characterized. The proteomic data allow recommendation of skeletal muscle protein troponin I (TnI) as a potential thermally stable and species-specific biomarker of mammalian muscle tissues in raw meat and meat products. A technique for the quantification of TnI is proposed. It includes sample preparation (extraction combined with heat treatment) and sandwich enzyme-linked immunosorbent assay. The technique had a TnI detection limit of 4.8 ng/ml and a range of quantifiable measurements from 8.7 to 52 ng/ml. The technique was suitable to detect TnI in mammalian meat (beef, pork, lamb, and horse) and distinguished these samples from poultry meat (chicken, turkey, and duck). The developed protocol was used to characterize meat-based products, including various kinds of sausages. TnI values estimated for pork and beef samples by ELISA were comparable with those of proteomic analysis. Thus, the quantitative study of TnI may be considered as a convenient way to assess the content of mammalian muscle tissues in various meat products.

Acknowledgments: *This investigation was financially supported by the Russian Scientific Foundation (project No 14-16-00149).*

MO16

Differentiation of fresh orange juice prepared by Merlin cultivar according to geographical origin based on organic acid and sugar content using chromatographic and chemometric analyses

I.K. Karabagias[1], C. Nikolaou[1], I. Gatzias[1], S. Kontakos[2], A. Badeka[1] and M.G. Kontominas[1,3]

[1] Laboratory of Food Chemistry Department of Chemistry University of Ioannina, Ioannina-45110 Greece
[b] Democritus University of Thrace, Department of Social Administration and Political Science, Komotini- 69100, Greece
[c] Department of Chemistry, American University in Cairo, New Cairo-11835, Egypt.

E-mail: mkontomi@cc.uoi.gr

The aim of the present study was to differentiate fresh orange juice prepared from oranges of the Merlin cultivar (Washington Navel) according to geographical origin, based on the combination of organic acid and sugar content using multivariate analysis of variance (MANOVA) and linear discriminant analysis (LDA). For this purpose, oranges were collected during the 2013 harvesting period from 4 different regions in Greece (Messinia, Arta, Rhodes, and Hania) producing, among other regions, the Merlin cultivar. The analysis of organic acids (citric, malic, tartaric, fumaric, oxalic) was performed using high pressure liquid chromatography (HPLC) with a UV detector at λ=210 nm. Additionally, sugars (fructose and glucose) were determined using HPLC coupled to a refractive index (RI) detector and a thermostated oven at 80^0C. Results of MANOVA showed oxalic acid, malic acid, fructose, and glucose to be significant for the differentiation of juice geographical origin. Application of LDA to these four parameters provided a correct classification rate of 83.3 % (cross validation method) for orange juice originating from Merlin oranges of the above four regions.

Monday 21 September 2015

Royal Cruise Hall-A

Chair: L. Ebdon, A. Calokerinos

Spectrometry 1

Invited lecture

Methods to identify and conquer matrix and spectral interferences in ICP emission spectrometry

G.M. Hieftje, G. Chan, Y. Cheung and A.J. Schwartz

Indiana University, Department of Chemistry, 800 East Kirkwood Ave.,
Bloomington IN 47405 USA

E-mail: Hieftje@indiana.edu

IL09

Elemental analysis of foods and associated products is complicated by the range of sample matrices that are encountered. As a result, matrix interferences are of considerable concern. Such interferences arise when a given concentration of a target element, say selenium, produces a different signal when it is present, for example, in yeast or a plant extract. In these cases, calibration based on simple standard solutions fails. These errors are generally caused by matrix-dependent differences in the efficiency with which atoms and ions are generated and excited in the plasma. Such problems are particularly acute when ICP emission is viewed in an end-on fashion; in this mode, signals are higher and precision is better, but matrix interferences are worse, so recognizing them is even more critical. The errors are also usually worse in the analysis of organic samples.

We have been active in the development and application of novel methods to detect matrix interferences and, when they exist, to correct them. Our recent effort involves measuring either the spatial distribution of analyte emission or the effect of dilution on the magnitude of interference. Because the ICP is spatially heterogeneous, especially in an end-on observation mode, the magnitude of an interference changes from one plasma location to another. Indeed, even with a fixed analyte and interferent concentration, the effect can change from a signal enhancement in one location to a suppression in another. The interference-recognition method is then straightforward: a calibration curve (emission intensity vs. concentration) is created at a number of spatial locations in the ICP by using a series of solutions of known concentration. The emission signal from an unknown sample is then obtained at each of those locations and its apparent concentration determined at each location by reference to the corresponding calibration curve. If the sample behaves in the same way as the standards, the determined concentrations will be the same for all spatial locations. If the determined concentrations differ, a matrix interference clearly exists. The dilution-based method is similarly straightforward; because different analyte elements are affected dissimilarly by a matrix interferent, the degree of matrix-induced signal enhancement or suppression changes from one element to another during dilution. Ratioing two analyte signals as dilution proceeds then yields a constant value in the absence of an interferent but a changing value when an interference is present.

Methods of adapting these interference-correction methods to existing ICP emission spectrometers will be considered.

Elemental depth profiling with nanometer resolution using a novel laboratory set-up in the soft X-Ray range

J. Baumann[1], C. Herzog[1], M. Spanier[1], D. Grötzsch[1], L. Lühl[1], K. Witte[1], A. Jonas[1], S. Günther[1], F. Förste[1], R. Hartmann[2], M. Huth[2], D. Kalok[2], B. Steigenhöfer[2], M. Krämer[5], T. Holz[5], R. Dietsch[5], L. Strüder[2,3,4], B. Kanngießer[1], I. Mantouvalou[1]

[1]Institute for Optics and Atomic Physics, Technical University of Berlin, 10623 Berlin, Germany,
[2]PNSensor GmbH, Römerstraße 28, 80803 München, Germany
[3]University of Siegen, Department of Physics, Walter-Flex-Straße 3, 57068 Siegen, Germany
[4]Max-Planck-Institut für extraterrestrische Physik, Gießenbachstr., 85748 Garching, Germany
[5]AXO Dresden GmbH, Gasanstaltstr. 8b 01237 Dresden, Germany

E-mail: jonas.baumann@physik.tu-berlin.de

MO17

X-ray fluorescence methods are powerful tools for the non-destructive, quantitative analysis of various samples. Working in the soft X-ray range and using angle resolved measurements gives access to the depth distribution of light elements with nm-resolution in e.g. transistor gate stacks or ultra-shallow junctions [1,2]. Unfortunately, this technique is limited to a small community only, since highly brilliant soft X-ray sources, e.g. synchrotron facilities, are rare.

We present a novel laboratory set-up for scanning-free grazing emission X-ray fluorescence (GEXRF) in the soft X-ray range, utilizing a laser produced plasma [3] as excitation source. The X-ray fluorescence of a carbon-nickel multilayer (ML) sample is detected with a pn-CCD of PNSensor GmbH [4], used as energy dispersive area detector. Simulations of the GEXRF profile of the ML sample predict a prominent feature, whose position is strongly dependent on the bi-layer thickness. This feature is clearly visible in the measurements and allowed to determine the thickness gradient of the ML sample.

The presented results demonstrate the feasibility of laboratory GEXRF measurements in the soft X-ray range for the first time. This method might in the future allow a wider community to perform quantitative, non-destructive and high precision depth analysis and thus help in the development of novel nanoscaled materials.

References

[1] M. Müller, P. Hönicke, B. Detlefs and C. Fleischmann, *Materials* 7 (2014) 3147–3159.
[2] Y. Kayser, D. Banaś, W. Cao, J.-Cl. Dousse et al., *X-Ray Spectrom.* 41 (2012) 98–104.
[3] I. Mantouvalou, K. Witte, D. Grötzsch, M. Neitzel, S. Günther, J. Baumann, R. Jung, H. Stiel, B. Kanngießer and W. Sandner, *Rev. Sci. Instrum.* 86 (2015) 035116.
[4] L. Strüder, U. Briel, K. Dennerl, R. Hartmann, E. Kendziorra et al., *A&A* 365 (2001), L18..

Identification and quantification of six polyvinyl chloride plasticizers by proton nuclear magnetic resonance in infusion medical devices

F. Feutry[1], S. Genay[1], M. Masse[1], C. Barthélémy[1], V. Sautou[2], B. Décaudin[1], P. Odou[1] and N. Azaroual[1]

[1] Univ Lille, EA GRITA, F-59000 Lille, France
[2] Clermont University, EA 4676 C-Biosenss, 63 000 Clermont-Ferrand, France

E-mail: frederic.feutry@gmail.com

MO18

Introduction: Until 2010, DEHP was the almost used plasticizer for medical devices (MD) made in polyvinyl chloride (PVC). Since its use was restricted because of reprotoxic risk, manufacturers had switch to alternative plasticizers. In a national project context (Assessment and Risk management of Medical Devices, ARMED) supported by the French national agency of drug safety (ANSM), we evaluated the use of proton nuclear magnetic resonance (NMR) to identify and quantify six mainly used alternative plasticizers: TOTM, DINP, DINCH, DEHA, ATBC, DEHT while ensuring the lack of DEHP in infusion medical devices.
Materials and Methods: NMR spectra of pure plasticizers dissolved in deuterated chloroform (10 mg in 600 µL of $CDCl_3$) were recorded on an AVANCE II 500 MHz spectrometer (Bruker Biospin, France) in order to determine characteristic resonances and allow identification and quantification using external standard (3-trimethylsilyl 2,2',3,3'-tetradeuteroproprionic acid (TMSP-d_4)). Six PVC MD were analyzed in blind after two hours extraction in $CDCl_3$ (piece of 10 mg in 800µL). Results of identification and quantification were compared to data (main plasticizer and concentration) given by the MD manufacturer.
Results: Each plasticizer presented specific resonances (Figure 1). For the 6 MD, main plasticizer was identified and quantified with 12.6, 1.3, 5.8, 9.6, 0.9, and 0.6% of relative error regarding theoretical concentration. Moreover, minority plasticizers were discovered in 4 over the 6 MD.

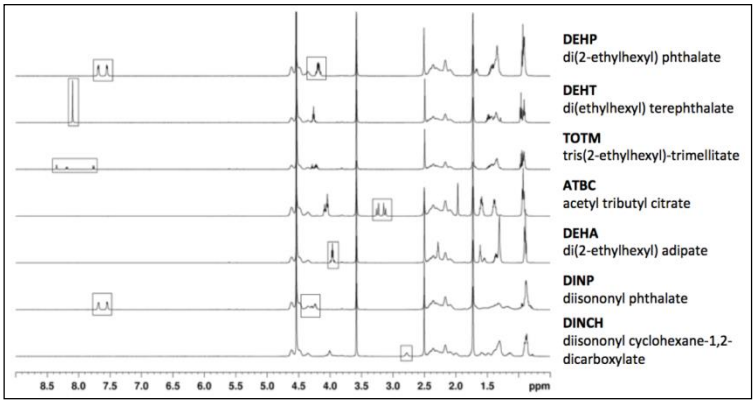


Fig. 1: Plasticizers specific resonances

Conclusion: This study demonstrated that NMR could be a helpful analytical method to identify and quantify plasticizers in medical devices.

Development of immunosensors based on optical waveguide lightmode spectroscopy (OWLS) technique for determining active substance in herbs

N. Adányi[1], K. Majer-Baranyi[1], E. Takács[2], B. Wang[3], I. Szendrő[4], A. Székács[2]

[1] Food Science Research Institute, National Agricultural Research and Innovation Centre, Hungary
[2] Agro-Enviromental Research Institute, National Agricultural Research and Innovation Centre, Hungary
[3] College of Agronomy and Biotechnology, China Agricultural University, Beijing, China
[4] MicroVacuum Ltd. H-1147 Budapest Kerékgyártó u. 10, Hungary

E-mail: n.adanyi@cfri.hu

MO19

An alarming number of alerting or warning signals concerning the quantity of the active ingredients or the presence of unauthorised substances originated from herb infusions or herbal supplement products have been announced lately in the European Union due to the efficient action of the Rapid Alert System for Food and Feed (RASFF). To facilitate such analyses, a new type immunosensor based on OWLS detection was investigated for the quick and reliable quantification of special active substances derived from herbs. Artemisinin is a sesquiterpene lactone antimalarial drug active ingredient derived from the sweet wormwood plant *Artemisia annua*, distilled from dried leaves or flower clusters. There are several synthetic derivatives of artemisinin also used for the treatment of malaria, including artesunate and artemether. Moreover it has been shown in laboratory assays, that these compounds also may be useful as anticancer agents. To determine these biologically effective subtances a novel immunosensor was investigated based on OWLS detection. The OWLS technique as a label-free immunosensor has been successfully applied for the detection of a number of different compounds in both competitive and in direct assays. In order to modify the sensitised surfaces to be regenerable, so that the sensor can be applied several times, the antigen or the antibody is immobilized on the surface by covalent attachment to the silanized surface. When measuring in direct manner the appropriate anti-artemether serum was immobilized on the sensor surface and the linear measuring range was determined. During competitive measurement the protein conjugate of artemether was immobilized on the waveguide surface. Standard solutions containing different amount of standard were mixed with antibodies of appropriate concentration, the mixture was incubated and injected into the flow injection analysis system of OWLS. Binding of the antibodies in the sample to the coated surface is competed for with the free antigen in the sample and only antibodies remained in free form in the mixture binds to immobilized antigen-conjugates. The amount of antibodies bound to the surface of the chip is inversely proportional to the active substance content in the samples. The dynamic measuring range and the relative substrate specificity of the anti-artemether serum on artemisinin and its derivatives were studied. Herbs of different origin and herbal supplement products were analysed using the newly developed method and a correlation was studied with reference method.

Acknowledgements: *This research was executed in the framework of the EU-project SPICED (Grant Agreement: 312631) with the financial support from the 7th Framework Programme of the European Union and in the scope of the Hungarian-Chinese bilateral project TET-12-CN-005C9251. This publication reflects the views only of the authors, and the European Commission cannot be held responsible for any use which may be made of the information contained therein.*

Chemiluminometric biosensor for genotyping of single-nucleotide polymorphisms in methylenetetrahydrofolate reductase (MTHFR) gene

E.M. Spyrou[1], D.P. Kalogianni[1], S.S. Tragoulias[1], P.C. Ioannou[2] and Th. K. Christopoulos[1]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504.
[2]Department of Chemistry, University of Athens, Athens, Greece 15771.

E-mail: tchrist@upatras.gr

MO20

Single nucleotide polymorphisms (SNPs) are single-base changes in the genome and constitute the most common type of human DNA variation. Because SNPs may affect gene function, they are emerging as new biomarkers for diagnosis of disease, assessment of genetic predisposition to diseases and pharmacogenetic testing. Methylenetetrahydrofolate reductase (MTHFR) is a key enzyme in the folate metabolism and catalyzes the conversion of 5,10-methylenetetrahydrofolate to 5-methyl-tetrahydrofolate, a cosubstrate for homocysteine remethylation to methionine. The C677T SNP is a common polymorphism in MTHFR gene. Individuals with 677CC genotype are 'normal'. Homozygotes with the 677TT genotype and heterozygotes (677CT) have significantly decreased MTHFR activity. Reduced MTHFR activity leads to hyperhomocysteinemia, which is associated with cardiovascular disease. In this context, we present the development of a rapid chemiluminometric biosensor for the genotyping of C677T SNP in MTHFR. The method comprises the following steps. *(a)* Genomic DNA isolation from whole blood, *(b)* Amplification of the DNA segment that flanks the polymorphism by the polymerase chain reaction (PCR) (a 90-min reaction). *(c)* Allele discrimination by a specific primer extension reaction (15 min). *(d)* Detection of the extension products by the dipstick-type chemiluminometric biosensor (20 min). The biosensor is based on a solid-phase DNA hybridization assay using peroxidase as reporter along with a chemiluminogenic substrate. A digital camera was used as a light detector. A 100-ng quantity of genomic DNA was used for amplification and the PCR produced a 423-bp fragment, as confirmed by agarose gel electrophoresis. An amount of 100 fmol of PCR product was introduced directly in the extension reaction without prior purification. A 5-μL aliquot of the extension reaction product was applied directly to the biosensor without prior treatment. The sensor was tested with samples of known genotype, including normal, heterozygote and homozygote for the mutation. In all cases the biosensor gave accurate results. The method is simple and rapid. The use of a digital camera, as a detector, eliminates the need for costly equipment and highly qualified personel.

Microfluidics tubing system for mercury detection utilizing fluorescent sensor nanoparticles

J. Bell, E. Climent, M. Albrecht and K. Rurack

Department 1 Analytical Chemistry; Reference Materials, BAM
Federal Institute for Materials Research and Testing,
Richard-Willstätter-Strasse 11, 12489 Berlin (Germany)

E-mail: jeremy.bell@bam.de

MO21

Currently, the development of portable devices to detect traces of chemical species by real time monitoring is a highly topical research area in the chemical sciences. Indeed, the lowering of standards for pollutants in drinking water requires the development of new technologies and devices. In this context, gated sensory nanoparticle systems for selective and sensitive recognition of targets such as heavy metal ions, small molecules or oligonucleotides are excellent candidates[1,2]. Provided that such sensory delivery systems are highly porous nanoparticles loaded with indicator dyes and capped with bulky stoppers that can be uncapped only by the designated analyte, an integration with a microfluidic tubing system designed for droplet-assisted liquid-liquid extraction enable separation of released from still particle-confined dye by phase-transfer extraction and subsequent selective detection by fluorescence. The incorporation in a simple microfluidic tubing system is an innovative way towards the realization of a sensor for trace analysis of target molecules in real time.

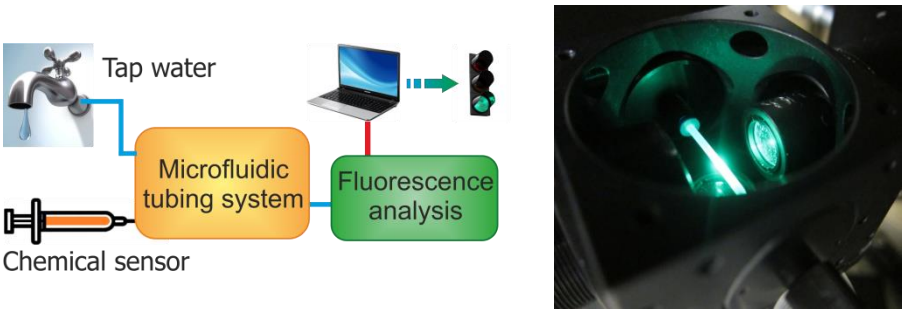


Fig. 1. Microfluidics fluorescent sensor scheme and view of the miniaturized fluorescence unit.

References

[1] E.Climent, R.Martinez-Manez, F.Sancenon, M.D.Marcos, J.Soto, A.Maquieira, P.Amoros, *Angewandte Chemie International Edition*, 49 (2010) 7281–7283.
[2] E.Climent,; M. D.Marcos,; R.Martinez-Manez,; F.Sancenon,; J.Soto,; K.Rurack,; P.Amoros, *Angewandte Chemie International Edition*, 48 (2009) 8519–8522.

Monday 21 September 2015

Royal Cruise Hall-A

Chair: M. Ochsenkühn-Petropoulou, J. Barek

Electrochemistry 1

Invited lecture

Voltammetric sensors in stripping procedures – past and present

A. Bobrowski

AGH University of Science and Technology, Department of Building Materials Technology, Faculty of Materials Science and Ceramics, Kraków, POLAND

E-mail: abobrow@agh.edu.pl

Stripping voltammetry has long been recognized as a very powerful technique for the determination of trace metals in a wide range of samples. Its practicability, precision, and selectivity are comparable with those of spectrometric techniques. However, stripping voltammetry outperforms the latter in on-site applications. The detection limits reported for various metals are in the ppb or ppt range. The success of the voltammetric sensing procedure depends mainly on the proper choice of the working electrode. This is because its ability to accumulate the analyte determines the sensitivity of the method. The main criterion of the selection of the proper working electrode is the available potential window. A variety of conductive materials have been used for the preparation of working electrodes [1]. Among them, a special place is held by two kinds of mercury electrodes – hanging mercury drop and film - because of their excellent voltammetric performance, and in particular their high overpotential of hydrogen reduction. The significant drawbacks of mercury electrodes, however, are electrode material toxicity and the instability of liquid mercury films. To overcome these disadvantages, less toxic mercury-containing materials have been used, such as amalgams and amalgam film electrodes. Moreover, numerous electrode materials with performance more or less similar to that of mercury have been proposed. Electrodes composed of films of metals such as bismuth, antimony, tin, and lead appear to be especially promising substitutes for mercury electrodes. Bismuth film electrodes were introduced to voltammetric practice in 2000 [2]. From the very beginning they have been successfully applied for anodic, adsorptive, cathodic and catalytic voltammetric stripping determinations of trace amounts of inorganic cations in various natural matrices [3-5].

In this lecture selected electrode materials and electrode designs (bulk electrodes, screen-printed electrodes) used for voltammetric sensing purposes will be presented. New procedures of activation and regeneration of the solid electrode surface between subsequent measurements will also be discussed.

References

[1] L.M. Moretto, K. Kalcher, eds., Environmental Analysis by Electrochemical Sensors and Biosensors, Springer, New York 2014
[2] J. Wang, J. Lu, S.B. Hocevar, P.A.M. Farias, B. Ogorevc, Anal. Chem., 72 (2000) 3218 - 3222.
[3] A. Economou, Trends Anal. Chem., 24 (2005) 334 - 340.
[4] I. Svancara, C. Prior, S. B. Hocevar, J. Wang, Electroanalysis, 22 (2010) 1405-1420.
[5] A. Bobrowski, J. Zarebski, Curr. Anal. Chem., 4 (2008) 191-201.

Adsorptive stripping voltammetry of Cr(VI) in the presence of pyrogallol red using electrodes of HgFE, BiFE and SbFE.

J.M. Navia, V. Arancibia, M. Gómez, C. Rojas and C. Nuñez

Pontificia Universidad Católica de Chile. Chemistry Faculty. Vicuña Mackenna 4860. Macul, Santiago de Chile. Phone: +56226864723

E-mail: darancim@uc.cl

MO22

Contamination of natural waters with chromium can be caused by anthropogenic sources such as leather tanning, pigment production, electroplating industry, and rinse waters, which mostly contain Cr(III) and/or Cr(VI). The toxicity of these two forms differs considerably: while Cr(III) is considered essential in mammals for the maintenance of glucose, lipid and protein metabolism for many living organisms, Cr(VI) species are known to be toxic and carcinogenic. Sea water contains between 0.1 and 0.5 μg L^{-1} and unpolluted river water from 0.3 to 0.6 μg L^{-1} [1]. Since the concentration of chromium, mainly Cr(VI), is very low in many natural waters, a highly sensitive and selective method is required for its analysis and speciation. Adsorptive stripping voltammetry (AdSV) is a useful technique to determine trace metals since it combines excellent sensitivity, selectivity, accuracy and precision with low instrumentation cost. The sensitivity and selectivity depend principally of the working electrode. The present study describes an adsorptive stripping procedure for Cr(VI) in the presence of pyrogallol red (PGR) using plating electrodes prepared with Hg, Bi and Sb. The method is based on the previous reduction of Cr(VI) to Cr(III) at the electrode surface, its complexation with PGR, and the later reduction of Cr^{III}–PGR to Cr^{II}–PGR. The effects of various operational parameters such as pH, ligand concentration (C_{PGR}), accumulation potential and time (E_{ads}, t_{ads}) were optimized. Under the best experimental conditions (pH 4.5; C_{PGR} 1.2 μmol L^{-1}; E_{ads} −0.60 V and t_{ads} 30 s), the peak current is proportional to the total Cr concentration up to 20.0; 35.0 and 10.0 μg L^{-1} with a 3σ detection limit of 0.7; 0.9 and 2.3 μg L^{-1}. for HgFE, BiFE and SbFE respectively. The method was validated using synthetic sea water (ASTM D665) spiked with Cr(VI) and Cr(III). With HgFE electrode and applying E_{ads} of −0.10 V is possible to determine Cr(VI) in the presence of Cr(III), with BiFE and SbFE only is possible to determine total chromium.

The authors acknowledge gratefully the financial support of Fondecyt under Regular Project 1130081.

References

[1] European Community Directive 80/778/EEC, L229/20. D48..

High sensitive determination of v(v) by catalytic adsorptive stripping voltammetry. Effect of sulfonic substituted ligand

C. Rojas-Romo, V. Arancibia

Laboratory of Inorganic Chemistry, Pontificia Universidad Católica de Chile, Santiago, Chile

E-mail: crrojas2@uc.cl

MO23

In the present work were studied quercetin (Q) and quercetin sulfonic acid (QS) as complexing agents for catalytic adsorptive stripping voltammetric determination of vanadium (V) in water and urine samples.
Experimental parameters were optimized; pH, ligand and $KBrO_3$ concentration, potential and time of accumulation. Optimal conditions for Q were pH:5,0; $CKBrO_3$: 10,0 mmol L^{-1}; CQ: 1,5 µmol L^{-1}; Eacc: 0,1 V; tacc: 30 s and for QS were pH:6,7; $CKBrO_3$: 10,0 mmol L^{-1}; CQS: 3,0 µmol L^{-1}; Eacc: 0,1 V; tacc: 30 s. Under optimal experimental parameters calibration plots were constructed (Figure 1), linear range and detection limit were determined.
For Q the linearity is maintained until 1,6 µg L-1, 3σ detection limit was 2,9 ng L^{-1} and a repeatability of 3,4% (n = 9; CV(V): 0,1 µg L^{-1}) with 30 s of accumulation time.
For QS the linearity is maintained until 0,7 µg L^{-1}, 3σ detection limit was 0,25 ng L^{-1} and a repeatability of 1,7% (n = 9; CV(V): 0,1 µg L^{-1}) with 30 s of accumulation time. The use of quercetin sulfonic acid as chelating agent for V(V) determination allows the development of a high sensitive methodology. In fact, it is the most sensitive reported methodology to date.
Hence, the development methodology using a ligand with sulfonic group presented a higher sensibility and a lower detection limit than no substituted ligand. Others results using ligands with a sulfonic groups showed an increase of sensibility for metallic ions determination by AdSV.

Acknowledgements: Authors are gratefully acknowledge for financial support FONDECYT under Regular Project No. 1130081 and CONICYT by doctoral fellowship (No. 21120190).

How alive can electrochemical DNA biosensors be?

V. Vyskočil, Z. Krejčová, K. Stávková, and A. Hájková

Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Hlavova 2030/8, CZ-12843 Prague 2, Czech Republic

E-mail: vlastimil.vyskocil@natur.cuni.cz

MO24

In the last five years, our attention has been paid to the development of electrochemical DNA biosensors enabling investigation of supramolecular interactions between selected genotoxic organic compounds (nitro, amino, and oxo derivatives of polycyclic aromatic hydrocarbons) and double-stranded DNA (dsDNA). The motivation of this research was to find relationships between their genotoxic effects described on the basis of biological experiments *in vivo* [1] and interactions observed electrochemically *in vitro* using our DNA biosensors. Various electrochemical transducers (working electrodes) were used for surface immobilization of dsDNA in order to allow obtaining comprehensive electrochemical data in both cathodic and anodic potential regions: a hanging mercury drop electrode, a silver solid amalgam electrode, a glassy carbon electrode [2,3], a screen-printed carbon electrode [4], and a microcrystalline natural graphite–polystyrene composite film electrode [5].

It will be shown in this contribution that electrochemical transformation of the studied compounds can, to some extent, simulate their fate in living systems during bioactivation [1,4]. Moreover, such transformation, when performed at the surface of the DNA biosensor, enables the formed intermediates to interact directly with the dsDNA structure. Thus, the direct interactions of both parent compounds and their metabolites with dsDNA can be studied. The complex electrochemical data obtained then help us to better understand the events causing dsDNA damage. Although there are still some limitations of electrochemical DNA biosensors (*e.g.*, certain enzymatic reactions, forming analyte–dsDNA covalent adducts *in vivo* [1], cannot be performed *in vitro* so easily), they surely represent very useful tools to bring *in vivo* and *in vitro* experiments closer together.

V.V. thanks the Grant Agency of the Czech Republic (Project GP13-23337P) and co-authors thank the Grant Agency of the Charles University in Prague (Projects GAUK 140214/2014/B-CH/PrF (Z.K.) and GAUK 430214/2014/B-CH/PrF (K.S. and A.H.)) for the financial support.

References

[1] L. Möller, *Environmental Health Perspectives*, 102 (1994) 139-146.
[2] K. Stávková and V. Vyskočil, *Chemické Listy*, 108 (2014) s262-s265.
[3] A. Hájková, J. Barek, and V. Vyskočil, *Electroanalysis*, 27 (2015) 101-110.
[4] V. Vyskočil, J. Labuda, and J. Barek, *Analytical and Bioanalytical Chemistry*, 397 (2010) 233-241.
[5] V. Vyskočil and J. Barek, *Procedia Chemistry*, 6 (2012) 52-59.

Development of electrochemical sensing devices for caffeine detection and immunosensor applications in the food industry

G.F. Duffy and E.J. Moore

Sensing and Separation Group, Chemistry Department and Life Science Interface Group, Tyndall National Institute, University College Cork

E-mail: gerard.duffy@tyndall.ie

MO25

The use of sensor technology in food analysis has gained a large amount of interest in recent years. In this work, two different sensing strategies are outlined. Firstly, a chemical sensor for the detection of caffeine in real samples has been developed. As caffeine is an electrochemically active compound it can be detected directly using voltammetric methods. The vast majority of electrochemical methods to detect caffeine have used conventional electrodes such glassy carbon and boron doped diamond electrodes. However, this work makes use of screen printed carbon electrodes which have a number of advantages, primarily their low cost and the lack of time consuming pre-treatment methods required before analysis. In order to improve sensor performance graphene oxide and nafion were used to modify the sensor surface. This allowed for a significant decrease in the limit of detection observed.

The second type of sensor designed in this work was an electrochemical immunosensor for the detection of mouse IgG as a model analyte. An optimised competitive ELISA protocol was first developed. This protocol was then transferred to screen printed electrodes which allowed for the detection of mouse IgG electrochemically. The sensitivity of an electrochemical immunosensor depends on a number of factors: well orientated antibody immobilisation onto the electrode surface, correct choice of electrochemical technique and efficient oxidation or reduction of the enzyme/substrate product. With this in mind, graphene oxide and multiwalled carbon nanotubes were used to modify the electrode surface with the aim of improving electrode performance. This work is a precursor to the detection of mycotoxins in milk and grain samples.

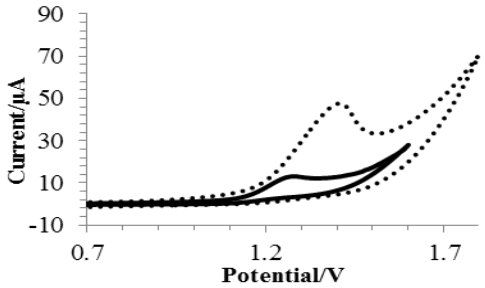


Fig.1. Electrochemical detection of caffeine using a nafion modified screen printed electrode (dotted line) compared to bare electrode

Chalcones as multifunctional antioxidants: a study of their interaction with copper ions

O. Serifi[1,2], M. Ochsenkühn-Petropoulou[1], A. Karantonis[3], A. Detsi[2]

[1]Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, NTUA
[2]Laboratory of Organic Chemistry, School of Chemical Engineering, NTUA
[3]Department of Materials Science and Engineering, School of Chemical Engineering, NTUA

E-mail : oserifi@mail.ntua.gr

MO26

Oxidative stress is a multifactorial process and and a wide range of stressors, such Reactive Oxygen Species (*e.g.* oxygen-based radicals, peroxides), nitric oxide, peroxynitrite and free metal ions can play an important role in its expression. As a result, the antioxidant activity exhibited by endogenous or exogenous antioxidants can be owed to different mechanisms such as radical scavenging or chelation of metal. Chalcones are flavonoid precursors which possess a wide range of bioactivities such as antioxidant, antitumor, antibacterial and anti-inflammatory. In previous studies we have evaluated the ability of a series of 2'-hydroxy-chalcone analogues to effectively scavenge ROS (DPPH, HO, H_2O_2) and proved that they can act as powerful antioxidants [1]. The α,β-unsaturated carbonyl structure of 2'-hydroxy-chalcones can possibly act as a chelation site for adventitious metal ions that can cause oxidative stress, we have proceeded to the investigation of the interaction of 2'-hydroxy-chalcone analogues with Cu^{2+}. The study was implemented using electrochemical and spectroscopic techniques, namely cyclic voltammetry (CV) [2] differential pulse voltammetry (DPV) [3] and UV/Vis spectrometry [3]. The results (Fig.1) indicate that certain chalcone analogues exhibit remarkable capacity of complexing Cu^{+2} therefore chalcone analogues can be considered as 'multifunctional antioxidants'.

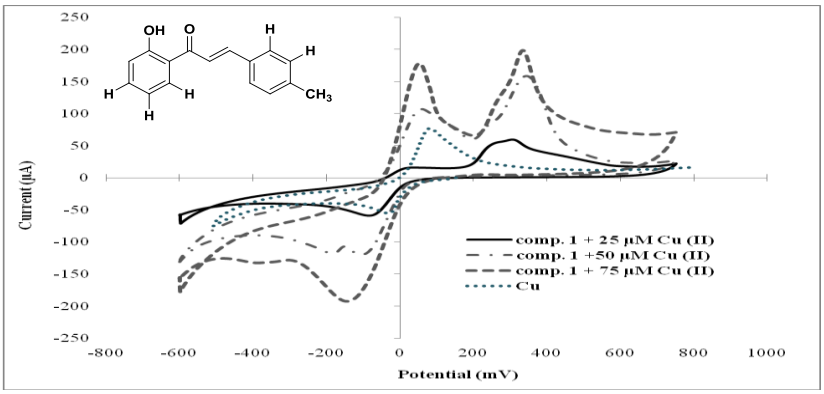


Fig 1. Cyclic voltammogram of chalcone 1 in the presence of increasing concentrations of Cu^{+2} ($Cu(NO_3)_2$), 25μM-75μM in 10mM MOPS buffer. $Cu(NO_3)_2$ (dotted), 25 μM in 10mM MOPS buffer.

References

[1] A. Detsi, M. Majdalani, C.A. Kontogiorgis, D. Hadjipavlou-Litina, P. Kefalas, Bioorg. Med. Chem. 17 (2009) 8073-8085.
[2] N. Shahabadi, N. H. Moghadam, Sprectochim. Acta, 99 (2012) 18-22.
C. A. Collins, F. H. Fry, A. L. Holme, A. Yiakouvaki, A. Al-Qenaei, C. Pourzand, C. Jacob, Org Biomol Chem., 8 (2005) 1541-1546.

Monday 21 September 2015

Royal Cruise Hall-B

Chair: E. Rosenberg, A. Gundlach-Graham, V. Sinanoglou, A. Vlessidis

Poster Session 1

Food Analysis

Spectrometry

Dispersive liquid–liquid microextraction method development for isolation and preconcentration of pesticide residues from alcoholic beverages

M. Andraščíková, M. Brišová and S. Hrouzková

Department of Analytical Chemistry, Faculty of Chemical and Food Technology Slovak University of Technology in Bratislava, Radlinského 9, 812 37, Bratislava, Slovak Republic

E-mail: maria.andrascikova@stuba.sk

P1-01

Current trends in sample preparation have focused on microextraction techniques using extremely low or no solvent consumption. Recently, a new microextraction method, dispersive liquid–liquid microextraction (DLLME), has been developed by Assai and co-workers [1] as an efficient sample preparation and preconcentration method. Essentially, DLLME consists in the rapid addition to an aqueous sample contained in a conical test tube a mixture of two selected solvents, few microliters of a waterimmiscible extractive solvent with higher density than water jointly with a dispersive solvent with high miscibility in both, extractant and water phases, in order to form a cloudy solution consisting of small droplets of extractive solvent which are dispersed throughout the aqueous phase. In consequence of the very large surface area formed between the two phases, hydrophobic solutes are rapidly and efficiently enriched in the extraction solvent and, after centrifugation, they can be determined in the phase settled at the bottom of the tube [2, 3].
The aim of this study was to develop dispersive liquid-liquid microextraction method for isolation and preconcentration of selected pesticides of different chemical groups from samples with some degree of alcohol. The effect of several extraction parameters, such as selection of extractive solvent, its volume and extraction time was tested. Four different extractive solvent (chloroform, tetrachloroethane, tetrachloromethane and toluene) and their combinations were evaluated for DLLME. The volume of selected extractive solvent and the salt addition was investigated. Finally, ultrasound and vortex assistance were compared in selected extraction time intervals.

Acknowledgements: This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Academy of Sciences (VEGA, project No. 1/0503/14) and by the Slovak Research and Development Agency under the contract No. APVV-0797-11.

References

[1] M. Rezaee, Y. Assadi, M.-R. M. Hosseini, E. Aghaee, F. Ahmadi and S. Berijani, *J. Chromatogr. A*, 1116 (2006) 1-9.
[2] S. C. Cunha and J. O. Fernandes, *Talanta*, 83 (2010) 117-125.
[3] M. Andraščíková, E. Matisová and S. Hrouzková. *Sep. Purif. Reviews*, 44 (2015) 1-18.

Analysis of volatile compounds in virgin olive oils from four cultivars using HS-SPME-GC

C.V. Antoniou and G.C. Koubouris

Institute of olive tree, subtropical crops and viticulture (IOSV), Agrokipio 73100, Chania, Greece

E-mail: xrysaa@yahoo.com

P1-02

The aim of this work was to develop a fast and simple analytical method for the determination of volatile organic compounds in olive oil samples.. The headspace-solid-phase microextraction (HS-SPME) and gas chromatography (with mass spectroscopy detector) was used for the determination of the volatile organic compounds. Solid phase microextraction (SPME) [1] is a fast, solventless procedure and does not require complex instrumentation.

In this study, the compounds that were determined were: 1-penten-3-one, 1-penten-3-ol, trans-2-pentenal, 3-pentanone, 1-pentanol, 1-hexanol, 3-hexanol, trans-2-hexen-1-al, cis-3-hexen-1-ol, hexanal. 2-Nonanone was used as internal standard. The SPME fiber 50/30 μm divinylbenzene/Carboxen/polydimethylsiloxane (DVB/CAR/PDMS) was used for the determination of the volatile compounds. The extraction parameters such as extraction temperature, extraction time, desorption time, salt effect and magnetic stirring were investigated. Also, the analytical parameters such as repeatability, linearity and detection limits were evaluated.

This method was applied for the determination of C5 and C6 volatile organic compounds in olive oil samples. The olive oil samples were from Koroneiki, Thiaki, Koutsourelia and Dafnelia cultivars. These cultivars, are grown under the same agronomic and climatic conditions in a specified area of the Institute of olive tree, subtropical crops and viticulture in Chania. The olive fruits were picked by hand during November 2014. The olive oil produced in a laboratory scale system where the malaxation of the paste was at 28 ºC for 30 min and no water was added during the olive oil extraction procedure.

Acknowledgments: This research project is funded under the Project *'Research & Technology Development Innovation Projects'*-AgroETAK, MIS 453350, in the framework of the Operational Program '*Human Resources Development'*. It is co-funded by the European Social Fund through the National Strategic Reference Framework (Research Funding Program 2007-2013) coordinated by the Hellenic Agricultural Organization – DEMETER (Institute of olive tree, subtropical crops and viticulture / Scientific supervisor: Dr. G.C. Koubouris).

References

[1] J. Pawliszyn, *Solid Phase Microextraction: Theory and Practice*, Wiley-VCH, New York (1997).

Sugar detection in sodas utilizing a fluorescent microfluidics sensor

J. Bell, P. Ashokkumar, M. Albrecht and K. Rurack

Department 1 Analytical Chemistry; Reference Materials, BAM
Federal Institute for Materials Research and Testing, Richard-Willstätter-Strasse 11, 12489 Berlin (Germany)

E-mail: jeremy.bell@bam.de

P1-03

Because of the globally increasing prevalence of diabetes, the need for accurate, efficient and at best miniaturized automated analytical systems for sugar detection is still urgent. The development of molecular probes for sugar based on boronic acid receptors offers an excellent alternative to the kinetically slow enzyme-based sugar sensors [1]. Moreover, by coupling such chelating units with rhodamines, fluorescein or BODIPY moieties, colorimetric and/or highly fluorescent sugar sensing schemes can be obtained [2, 3]. In this work, a boronic acid-functionalized BODIPY probe is described; it binds selectivity to fructose's adjacent diols to form cyclic boronate esters in partially aqueous solutions, with a broad pH range compatibility and a sensitivity in the micromolar range. To enhance the applicability of the fluorometric test in the sense described above, integration with a microfluidic sensor was achieved. The miniaturization of chemical analysis systems yields many functional and economical benefits such as low cost, ease of use, high stability and good portability. With similar selectivity and sensitivity, fructose was detected by fluorescence in real time in the chip, and an assay for the straightforward detection of sugar in sodas was achieved.

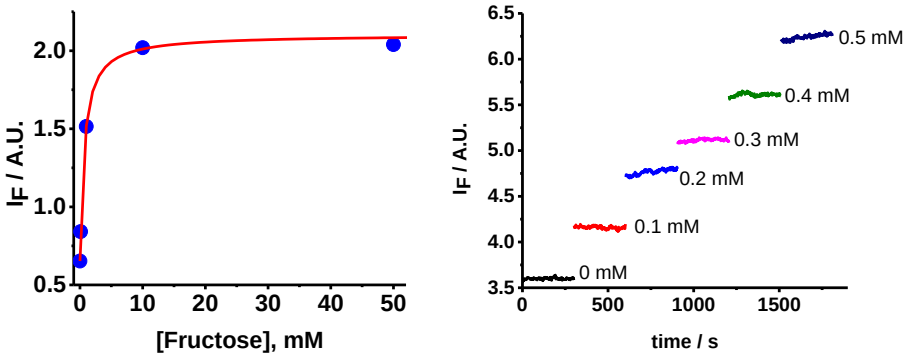


Fig. 1: Detection of fructose in H_2O/EtOH 7/3; v/v by the BODIPY probe in a cuvette (left) and inside a microfluidic chip (right)

References

[1] J. Yoon and A. W. Czarnik, *Journal of the American Chemical Society*, 114 (1992) 5874–5875.
[2] Y. Iwami, T. Yokozawa, W. Takayoshi and Y. Kanekiyo, *Talanta*, 85 (2011) 829–833
[3] J. Zhai, T. Pan, J. Zhu, Y. Xu, J. Chen, Y. Xie and Y. Qin, *Analytical Chemistry*, 84 (2012) 10214–10220.

Authentication of game meat through rare earth and trace element profile: The case of Limnos island wild rabbits

G. Danezis[1], A. C. Pappas[2], E. Zoidis[2], C. Papachristidis[1], C. Vavvas[2], G. Papadomichelakis[2], I. Hadjigeorgiou[2], V. Brusic[3] and C. A. Georgiou[1*]

[1]Chemistry Laboratory, Department of Food Science and Human nutrition &
[2]Department of Nutritional Physiology and Feeding, Faculty of Animal Science and Aquaculture, Agricultural University of Athens, 75 Iera Odos, 11855 Athens, Greece
[3]School of Science and Technology, Nazarbayev University, Astana, Kazakhstan

P1-04

E-mail: cag@aua.gr

Consumers are concerned about the meat they eat and accompanying claims on labelling e.g. wild versus farmed, geographical origin, organic versus conventional, processing-treatment. Moreover game meat is much more expensive in comparison to that from farmed animals. Species authentication is normally based on molecular techniques while origin authentication, as far as it refers to animals of the same genetic strain could be based on differences induced by feeding. This work shows that different feeding of wild animals induces clear differences in rare earth and trace element fingerprints. This study is the first effort for meat authentication by the rare earth element fingerprint. Moreover it is the very first work on game meat authentication through the elemental profile.

The content of trace and rare earth elements in meat beyond feed intake depends on various factors such as drinking water, pollution and soil composition, all of which depend on geographic origin. Although the feed of farmed animal could be transported from remote areas, wild animals' feed reflects the vegetation-pasture of a specific region particularly of the limited island space as in the case of Limnos. Useful discriminants for authenticity determination are especially those being not essential to animals and/or being toxic at higher levels, as their use in mineral supplementation is unlikely. In this respect the REEs fingerprint could be a very reliable authentication marker.

Elemental fingerprints were investigated for their potential to discriminate wild from commercial and backyard rabbit samples. Concentrations of rare earths Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y & Yb, actinides Th &U and trace elements Se, Zn, Mn, Mg, Pb, Fe, Cu, Co, Ca, As, Sb, Mo, Ni, Cd, Cr, V, Sr, Li, Be, Ti & Tl in 31 wild rabbits, 5 backyard rabbits from Limnos island and 12 commercial rabbits were analysed by ICP-MS. Tissue samples were from longitudinal dorsal muscle. Rare earth elements and actinides discriminate clearly wild from commercial rabbits. Wild rabbits presented higher Dy, Er, Eu, Ho, Lu, Th, Tm & Yb concentrations and lower Sc & U concentrations than commercial rabbits. Regarding trace elements, wild rabbits showed significantly higher As, Sb, Sr & V values while commercial rabbits higher Mg. The chemometric tools, such as Principal Component Analysis (PCA) & Support Vector Machine (SVM) that are used, presented very good discrimination between wild, backyard and commercial rabbits. These results demonstrate the usefulness of rare earths fingerprints as indicators for game meat authentication.

Rare earth elements & actinides accumulation patterns in game meat, backyard & commercial rabbits

G. Danezis[1], A. Tsagkaris[1], E. Zoidis[2], A.C. Pappas[2], C. Papachristidis[1], C. Vavvas[2], G. Papadomichelakis[2], I. Hadjigeorgiou[2], V. Brusic[3] and C.A. Georgiou[1*]

[1]Chemistry Laboratory, Department of Food Science and Human Nutrition &
[2]Department of Nutritional Physiology and Feeding, Faculty of Animal Science and Aquaculture, Agricultural University of Athens, 75 Iera Odos, 11855 Athens, Greece
[3]School of Science and Technology, Nazarbayev University, Astana, Kazakhstan

E-mail: cag@aua.gr

P1-05

REEs encompass a group of metals that are of strategic value being essential for all applications, involving magnets and cell phones, while production is spatially limited mostly to China. Emerging applications in food authentication involve REEs as indices of geographic origin. REEs fingerprint is characteristic of the growing region of plant derived foods and also animal meat grown on them. There are also a limited number of studies indicating positive effect on crop and animal productivity when fertilizing or using REEs as feed additives.

Inductively coupled plasma mass spectroscopy (ICP-MS) is almost exclusively used for REEs providing high-throughput, ultra-trace level analysis down to ppt.[1] The content of rare earth elements in animals depend on various factors such as feed intake, drinking water and pollution.

We surveyed 16 rare earth elements, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y & Yb and two actinides, Th & U in different tissues of 36 wild, 5 backyard rabbits from Limnos island and 12 commercial rabbits. Sampled tissues were longitudinal dorsal muscle, liver, blood and hair. This is the first study on REEs and actinides bioaccumulation in animals that are destined for human consumption. This work evaluates different feeding styles of the same species concerning bioaccumulation, fate and transport of REEs.

Tissue concentration patterns indicated that REEs and actinides accumulated to a greater extent in hair. Moreover, liver in wild and backyard rabbits presented higher REEs concentrations than muscle. These are in line with data on trace elements accumulation. It was revealed that for game meat, the Oddon-Harkins rule is valid. According this rule, the element with an even atomic number is more abundant than the next element with an odd atomic number. We have also found a concentration decrease on increasing atomic weight that is in line with the terrestrial distribution trend. Ce and La were the most abundant REEs in wild and backyard rabbits while in commercial rabbits Ce and Sc probably reflecting the feeding regime. This work reports an adequate data set of rare earth elements and actinides profile that adds to the very limited information in the published literature facilitating further work on meat authentication.

References

[1] C.A. Georgiou, G.P. Danezis, Elemental & Isotopic Mass Spectrometry, in Y. Pico (Ed.) Advanced Mass Spectrometry for Food Safety and Quality, *Comprehensive Analytical Chemistry*, Elsevier: Amsterdam, (2015) in press.

Monitoring of tin and aluminum release from food packaging to packaged food

P. Diviš and P. Šiler

Brno University of Technology, Faculty of chemistry, Materials Research Centre, Purkyňova 118, Brno 61200, Czech Republic

E-mail: divis@fch.vutbr.cz

P1-06

Tinplate cans and aluminum cans have several advantages over other food packaging material including light weight, compact packaging, low oxygen permeability etc. According to the available literature, up to 20 bilion tin cans and 60 bilion of aluminum cans are produced in Europe each year. As a result of the use of these cans for food and beverage packaging, it is obvious that some tin and aluminum will dissolve into the food content. Long-term consumption of food containing higher concentration of tin and aluminum may adversely affect central nervous system, kidney, liver and the overall human health [1, 2]. In this study tin and aluminum concentration in caned food and beverage was monitored using ICP-OES technique. In total 40 fruit samples, 28 energy drink samples and 22 bier samples in cans were analyzed and the results are presented. This study clearly showed that there is a need to pay attention to the issue of the interaction of the can with a packaged food, since increased concentrations of tin and aluminum in analyzed food samples were measured.

Aknowlwdgements: This work was financially supported by the project: Materials Research Centre at FCH BUT — Sustainability and Development, REG LO1211, with financial support from the National Programme for Sustainability I (Ministry of Education, Youth and Sports, Czech Republic)

References

[1] S. Blunden and T. Wallace, *Food and Chemical Toxicology*, 41 (2003) 1651-1662.
[2] T. Stahl, H. Taschan and H. Brunn, *Environmental Sciences Europe*, 23:37 (2011) 1-11.

Determination of taurine in energy drink by IC/PAD

H. Farkaš, J. Banić-Simičić, D. Ujsasi, A. Plahi Bognar and B. Marošanović

SP Laboratorija A.D., Industrijska 3, Bečej, Serbia

E-mail: splaboratorija@victoriagroup.rs

P1-07

Taurine,also known as 2-aminoethanesulfonic acid, is the main component of many energy drinks as a tonic medicine.Furthermore, it is different from most other amino acids becase it is not incorporated into proteins.Taurine is unusual among biological molecules in being a sulfonic acid, while the vast majority of biologically occurring acids contain the more weakly acidic carboxyl group.While taurine is sometimes called an amino acid, and indeed is an acid containing an amino group, it is not an amino acid in the usual biochemical meaning of the term, which refers to compounds containing both an amino and a carboxyl group. Nevertheless, it does play many important roles in the body.

A rapid and simple method for taurine determination in energy drink was developed by anion-exchange chromatography with integrated pulsed amperometric detection.

Sample preparation did not include derivatization step, only dilution of the sample with ultra pure water.

Mobile phase was ultra pure water, 250mM NaOH and 1M NaOAc for IC determination flowing under gradient elution.

Taurine was analysed with AminoPac PA10 column (2x250mm) and guard column (2x50mm) on Ion Chromatograph, ICS-5000, Dionex.

The recovery was in the range of 90,8 – 108,4%, the precision as standard deviation were 6,27%,the linearity as a coefficient of correlation value was 0,9991.The content of taurine measured in commercial energy drinks was in range of 400-4000mg/l.

In the period from 2012-2015 we have analyzed 109 samples with taurine content. In 2 of all analized samples taurine was below the limit of quantification, 9 of them had concentration in about 400mg/l and 98 of all samples had the taurine concentration in range of 3000-4000mg/l.

All the analyzed samples were in compliance with Serbian and EU regulation in which defined maximum concentration is 4000mg/l.

References

[1] T.R. Cataldi, G. Telesca, G. Bianco, *Anal Bioanal Chem*, 378 (2004) 804-810.

Sensitive determination of halogenated nitrogenous disinfection by-products in drinking water samples

Y. Kadmi[1,2], L. Favier[1,2], M. Gavrilescu[3,4], C. Vial[5,6] and D. Wolbert[1,2]

[1]Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France
[2]Université Européenne de Bretagne, France
[3]"Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Environmental Engineering and Management, 73 Prof. dr. docent Dimitrie Mangeron Str., Iasi 700050, Romania
[4]Academy of Romanian Scientists, 54 Splaiul Independentei, RO-050094 Bucharest, Romania
[5]Clermont Université, Université Blaise Pascal, Institut Pascal ; 24 avenue des Landais, BP 20206, 63174 Aubière cedex, France; E-mail: christophe.vial@univ-bpclermont.fr
[6]CNRS, UMR 6602, IP, 63171 Aubière, France

E-mail: lidia.favier@ensc-rennes.fr; yassine.kadmi@gmail.com

P1-08

Haloacetamides are a class of unregulated disinfection by products (DBPs) which have recently received considerable attention because of their high toxicity. Indeed, these compounds have been reported to be more cytotoxic and genotoxic than some of the currently regulated DBPs (e.g. haloacetic acids). One of the main factors limiting their study is the lack of sensitive and well-validated analytical methods for their identification and quantification. The aim of this study is to develop a simple, rapid and sensitive methodology for the detection and quantification of low levels of haloacetamides in different types of water samples. A novel method combining solid-phase extraction, ultra-performance liquid chromatography and tandem mass spectrometry (UPLC/MS/MS) was developed. Chromatographic separation was performed using an Acquity UPLC C18 column with a mobile phase consisting of acetonitrile and ultrapure water (90:10, v/v) at a flow rate of 400µL/min. The run time of the method was four minutes. Good linearity ($r^2 \geq 0.998$), precision (less than 4.5%) and acceptable accuracy (in the range of 99-103%) were obtained at all quality control levels. Good extraction recoveries, within the range of 99-101% were determined at different fortification levels and the relative standard deviations were less than 4%. The matrix effect was also investigated. The quantification limit was in the low (ng/L) range. The obtained results showed that the new developed analytical method is simple, highly sensitive, and accurate. Finally, this technique can be considered as an attractive and promising analytical tool for the screening of haloacetamides at ultra-trace levels in aqueous samples.

Simultaneous determination and quantification of polyphenol compounds, flavonoids, and oleuropein derivatives using the –OH ^{1}H-NMR spectral region: Optimization of experimental conditions and application to oregano and olive leaf extracts

P. Charisiadis[1], V.G. Kontogianni[1], C.G. Tsiafoulis[2,3], A.G. Tzakos[1] and I.P. Gerothanassis[1]

[1] Section of Organic Chemistry & Biochemistry, Department of Chemistry, University of Ioannina, Ioannina 45110 Greece
[2] NMR Center, University of Ioannina, Ioannina 45110 Greece
[3] Laboratory of Analytic Chemistry, Department of Chemistry, University of Ioannina 45110 Greece

E-mail: igeroth@uoi.gr

High resolution ^{1}H NMR spectroscopy of the –OH spectral region [1] has been employed as a rapid method for the simultaneous determination and quantification of polyphenol compounds, flavonoids, and oleuropein derivatives in two crude oregano and olive leaf extracts without any prior isolation step. The strategy is based on the highly deshielding characteristic chemical shift region of the –OH groups and their correlations in the proton–carbon heteronuclear multiple-bond correlation (^{1}H–^{13}C HMBC) NMR spectra [2-4] which allow the structure elucidation and quantification. A critical overview of experimental parameters that influence the resolution of the –OH groups is provided with emphasis on the effects of the dilution, the pH, the temperature, the nature of the solvent used for the extraction procedure and the NMR solvent effect. The combined use of optimized experimental conditions, the spiking with model and known compounds, through ^{1}H–^{13}C HMBC experiments, and ^{1}H –OH chemical shift index [5] allowed the rapid and simultaneous identification and quantification of polyphenol compounds, flavonoids and oleuropein derivatives. The quantitative results provided by ^{1}H NMR method are in agreement with those obtained with the use of LC-DAD and LC-SPE-NMR methods.

References

[1] P. Charisiadis, V. Exarchou, A.N. Troganis and I.P. Gerothanassis, *Chem. Commun.*, 46 (2010) 3589-3591.
[2] P. Charisiadis, A. Primikyri, V. Exarchou, A. Tzakos and I.P. Gerothanassis, *J. Nat. Prod.*, 74 (2011) 2462-2466.
[3] A.A. Nerantzaki, C.G. Tsiafoulis, P. Charisiadis, V.G. Kontogianni and I.P. Gerothanassis, *Anal. Chim. Acta*, 688 (2011) 54-60.
[4] P. Charisiadis, C. Tsiafoulis, V. Exarchou, A. Tzakos and I.P. Gerothanassis, *J. Agric. Food Chem.*, 60 (2012) 4508-4513.
[5] V.G. Kontogianni, P. Charisiadis, A. Primikyri, Ch.G. Pappas, V. Exarchou, A.G. Tzakos and I.P. Gerothanassis, *Org. Biomol. Chem.*, 11 (2013) 1013-1025; P. Charisiadis, V. Kontogianni, C.G. Tsiafoulis, A.G. Tzakos, I.P. Gerothanassis, *Molecules*, 19 (2014) 13643-13682.

DNA purification using a highly efficient microfluidic device with large capacity: Demonstration of DNA recovery from a few Salmonella bacteria cell lysate

A.S. Kastania[1], K. Tsougeni[1], G. Papadakis[2], E. Gizeli[2,3], G. Kokkoris[1] A. Tserepi[1] and E. Gogolides[1]

[1] Institute of Nanoscience and Nanotechnology, NCSR Demokritos,
15310 Aghia Paraskevi, Attiki, Greece
[2] Institute of Molecular Biology & Biotechnology, FO.R.T.H,
100 N. Plastira str, 70013 Heraklion, Greece
[3] Dept. of Biology, Univ. of Crete, Vassilika Vouton, Heraklion, Greece

E-mail: a.kastania@inn.demokritos.gr

P1-10

DNA purification is a basic step traditionally carried out in a laboratory prior to other procedures, such as PCR and DNA screening and is of high importance to all molecular diagnostics, including clinical tests, pathogen-analysis in food samples and environmental testing. In this work, a highly efficient and of high capacity polymeric microfluidic device for DNA purification is described. The DNA purification protocol used consists of three steps: i) DNA immobilization/precipitation, ii) cleaning and iii) elution of DNA. The microfluidc chip is fabricated via microfabrication processes on a poly(methyl methacrylate) (PMMA) substrate and is activated so that it contains -COOH groups on the chip surface. These carboxyl groups in combination with a buffer containing polyethylene glycol (PEG), NaCl and ethanol [1] have been shown to be able to bind DNA on the microchannel surface. The immobilization step is followed by intermediate cleaning with ethanol and elution with water. The chip was shown to be able to achieve high recovery for a large quantity of Salmonella DNA, indicating high DNA-capturing efficiency and, consequently, chip capacity. Salmonella DNA purification on chip was shown to be possible for as low as 5pg of pre-purified DNA and cell lysates corresponding to few cells. Chip evaluation was performed via absorbance measurements, PCR and gel electrophoresis.

These results indicate the high potential of the DNA-purification module in developing integrated platforms for genetic analysis. The system is currently used in the development of a Lab-on-Chip platform for food pathogen detection employing in addition to DNA purification, bacteria capture, lysis, PCR and DNA acoustic detection modules, as described within the EU project LOVE-FOOD (http://love-food-project.eu/doku.php?id=start).

References

[1] MA Witek, SD Liopis, A. Wheatley, RL. McCarley and S.A. Soper, *Nucleic Acids Research*, 34 (2006) e74.

Authentication tests for milk products based on a chemiluminometric hybridization assay

M. Kounelli[1], D.P. Kalogianni[1], P.C. Ioannou[2] and Th.K. Christopoulos[1,3]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504.
[2]Department of Chemistry, University of Athens, Athens, Greece 15771.
[3]Institute of Chemical Engineering and High Temperature Processes, Foundation of Research and Technology Hellas, GR-26504 Patras, Greece.

E-mail: kalogian@upatras.gr

P1-11

Milk and milk products like yogurt and cheese prepared from sheep and goat, experience an increasing demand from consumers and are recognized as healthy and natural products. These products are vulnerable to fraud by adulteration with other milk of lower cost. Thus, the development of new and sensitive analytical methods for the detection of the species-specific milk products is of a great need in order to protect the consumers from fraudulence. The present work focuses on the detection of specific DNA sequences for the identification of the animal origin of milk in foodstuffs. The method is based on the amplification of specific DNA sequences by the polymerase chain reaction (PCR) and a subsequent chemiluminometric hybridization assay carried out in polystyrene microtiter wells. More specifically, DNA is isolated from milk and yogurt produced from goat, sheep and cow and is subsequently subjected to PCR. The amplified DNA sequences are biotinylated, and are hybridized to species-specific oligonucleotide-probes, which carry a poly(dA) tail at the 3´ end. The hybrids are then captured by poly(dT) sequences immobilized on the microtiter wells and detected by a streptavidin-alkaline phosphatase conjugate (SA-ALP) via streptavidin-biotin interaction. The final step of the reaction is the addition of the chemiluminometric substrate of ALP PPD (4- methoxy-4-(3-phosphatephenyl) spiro[1,2-dioxetane-3,2'-adamantane], disodium salt) and the produced chemiluminescence is measured by a luminometer. The intensity of the chemiluminescence is linearly related to the concentration of the corresponding DNA sequence. The limit of detection of the proposed method was 1.4 pM for all DNA sequences. Finally, different mixtures of milk and yogurt from goat or sheep were prepared that contained various proportions of milk or yogurt from cow. As low as 0.01% of cow milk that was present in the milk products from sheep or goat was successfully detected.

Volatile compounds in probiotic dry-fermented sausages

M. Sidira[1,2], P. Kandylis[1], L. Bosnea[1], M. Kanellaki[1], T. Varzakas[3] and Y. Kourkoutas[2*]

[1]Food Biotechnology Group, Department of Chemistry, University of Patras, Patras, Greece.
[2]Applied Microbiology and Molecular Biotechnology Research Group, Department of Molecular
[3]Biology & Genetics, Democritus University of Thrace, Alexandroupolis, Greece.
[4]Department of Food Technology, Technological Educational Institute of Peloponnese, Kalamata, Greece.

P1-12

E-mail: ikourkou@mbg.duth.gr

The meat industry is seeking for functional starter cultures that meet health promoting, food safety, shelf-life, technological effectiveness and economic feasibility criteria. Such cultures may be also useful in reducing levels of nitrites and nitrates in fermented sausages, as their use is under discussion because of their contribution to the formation of health affecting nitrosamines.
Recently, Sidira et al. [1] investigated the effect of cell immobilization on wheat on the effective survival of *L. casei* ATCC 393 cells at levels for conferring a probiotic effect during ripening and during heat treatment of dry-fermented sausages. Noticeably, the probiotic properties of both free and immobilized *L. casei* ATCC 393 were previously assessed [2,3].
Apart from a beneficial to human health product, the development of a unique aromatic profile is an undeniable aim for the food industry. Thus, the aim of the present study was to investigate the effect of chemical preservatives, the probiotic culture (free or immobilized *Lactobacillus casei* ATCC 393 on wheat grains) and the ripening time on the generation of volatile compounds in probiotic dry-fermented sausages. Samples were collected after 1, 28 and 71 days of ripening and subjected to HS SPME GC/MS analysis. Esters, organic acids, alcohols and carbonyl compounds were the most important groups of volatiles identified. The content of esters, organic acids and total volatiles was significantly increased after 28 and 71 days of ripening in all products. In most cases, reduction of chemical preservatives resulted in significant increase of esters and organic acids during ripening, whereas the opposite effect was observed in alcohols at day 71 and in carbonyl compounds at days 28 and 71. Principal Component Analysis of the semi-quantitative data revealed that primarily the ripening process affected the volatile composition.
However, more research is required to understand the microbial interactions responsible for the biochemical changes occurring during ripening and the effect of the curing salts on volatiles.

References

[1] M. Sidira, A. Karapetsas, A. Galanis, M. Kanellaki and Y. Kourkoutas, Y. *Meat Science*, 96 (2014) 948-955.
[2] G. Saxami, P. Ypsilantis, M. Sidira, C. Simopoulos, Y. Kourkoutas and A. Galanis. *Anaerobe*, 18 (2012) 417-420.
[3] M. Sidira, A. Galanis, P. Ypsilantis, A. Karapetsas, Z. Progaki, C. Simopoulos and Y. Kourkoutas. *Journal of Molecular Microbiology and Biotechnology*, 19 (2010) 224-230.

Volatile compounds in probiotic yoghurts containing immobilized *Lactobacillus plantarum* 2035 on whey protein

M. Sidira[1], M. Kiourtzidis[1], N. Chorianopoulos[2], C. Tassou[2], S. Kaloutsas[4], G. Mitropoulou[2], T. Varzakas[3] and Y. Kourkoutas[2*]

[1]Applied Microbiology and Molecular Biotechnology Research Group, Department of Molecular Biology & Genetics, Democritus University of Thrace, Alexandroupolis, Greece.
[2]Institute of Technology of Agricultural Products, Hellenic Agricultural Organization DEMETER, 1 S. Venizelou Str, Lykovrisi, Athens, Greece.
[3]RODOPI SA Dairy Industry, 3rd km of Xanthi-Lagos National Rd, Xanthi, Greece.
[4]Department of Food Technology, Technological Educational Institute of Peloponnese, Kalamata, Greece.

E-mail: ikourkou@mbg.duth.gr

Currently, there is an upsurge of interest in developing novel foods containing probiotic microorganisms, such as bifidobacteria and lactic acid bacteria (LAB). Such functional foods demonstrate a great potential in promoting human health [1]. To deliver the health benefits, probiotics need to contain an adequate amount of live bacteria, able to survive the acidic conditions of the upper gastro-intestinal tract and proliferate in the intestine, a requirement that is not always fulfilled [2]. Since it is well established that cell immobilization enhances cell viability [3,4], the aim of the present study was to investigate the volatile compounds isolated by probiotic yoghurts produced using immobilized cells of *Lactobacillus plantarum* 2035 (kindly provided by the culture collection of Aristotle University of Thessaloniki) on whey protein, along with a commercial culture. For comparison reasons, yoghurts with free *L. plantarum* 2035 cells and with no probiotic culture were also prepared. All products using either bovine or ewe's milk were prepared by our industrial partner (RODOPI SA dairy industry). Organic acids, alcohols and carbonyl compounds were the most important groups of volatiles identified by HS SPME GC/MS analysis. In general, bovine milk resulted in higher content of organic acids and total volatiles, while fluctuations were observed in the rest volatile compounds. Principal Component Analysis showed that mainly the milk origin affected the profile of volatiles, rather than the probiotic culture or the storage time.

References

[1] G. Mitropoulou, V. Nedovic, A. Goyal and Kourkoutas, Y. *Journal of Nutrition and Metabolism*, (2013) http://dx.doi.org/10.1155/2013/716861.
[2] T.D. Boylston, C.G. Vinderola, H.B. Ghoddusi and J.A. Reinheimer, J. A. *International Dairy Journal*, 19 (2004) 315-387.
[3] T. Mattila-Sandholm, P. Myllarinen, R. Crittenden, G. Mogensen, R. Fonden and M. Saarela. *International Dairy Journal*, 12 (2002) 173-182.
[4] Y. Kourkoutas, V. Xolias, M. Kallis, E. Bezirtzoglou and M. Kanellaki. *Process Biochemistry*, 40, (2005) 411-416.

Optimization of industrial pretreatment of *Spirulina platensis* cyanobacterium

S. Papadaki, K. Kyriakopoulou and M. Krokida

School of Chemical Engineering, National Technical University of Athens,
Zografou Campus, GR-15700 Athens, Greece

E-mail: spcheng@central.ntua.gr

P1-14

Spirulina platensis is a cyanobacterium with known therapeutic properties to diabetes, arthritis, anaemia, cardiovascular diseases and cancer due to its content in antioxidant compounds (phycocyanin) and nutritious compounds (short chain PUFAs and chlorophylls). Phycocyanin is used as a functional ingredient into various food products to enhance their nutritional qualities acting as food colorant, antioxidant and emulsifier. Therefore, it can sufficiently replace or reduce the use of synthetic ones such as Brilliant blue FCF, BHA, BHT etc. Phycocyanin-rich Spirulina has already been marketed as a dietary supplement for human consumption [1, 2].

This study is a laboratory-scale application with potential scale up practice in drying process, a treatment stage that took place directly after the harvesting of the cultivation and shows great effect on the nutritional value of the final product. The dried methods that studied were: Accelerated Solar Drying, Freeze drying, Vacuum Drying and Spray drying [3, 4].

The dried Spirulina biomass was characterized evaluating spectrophotometrically the pigments content (total carotenoids, b-carotene, chlorophylls, asxtaxanthin, phycocyanin) [5-7]. Moreover, the carotenoids profile was evaluated using HPLC-DAD technique [8]. Finally, the antioxidant activity of the dried biomass was evaluated through DPPH assay.

References

[1] H.Shimamatsu, *Hydrobiologia*, 512 (2004) 39–44.
[2] M.K. Ü. Nal, *J. Food Sci*, .68 (2003) 1144-1148.
[3] P.C. Tiburcio, F.C.F. Galvez, L.J. Cruz and V.C. Gavino, J. *Appl. Phycol.*, 19 (2007) 719–726.
[4] A. Prasetyaningrum and M. Djaeni, *Inter. J. of Sci. and Eng.*, 3 (2012) 1–3.
[5] S.W. Jeffrey and G.F. Humphrey, *Biochem. Physiol. Pflanz* ,167(1975) 191–194.
[6] A. Ben-Amotz and M. Avron, *Plant Physiol.* 72 (1983) 593–597.
[7] S.Boussiba and A.E. Richmond, *Arch. Microbiol.* 120 (1979) 155–159.
[8] I.F. Strati and V. Oreopoulou, *Food Chem.* 129 (2011) 747–752.

Impact of feed supplementation with different natural antioxidants on fatty acid profile and color parameters of egg yolk lipid fraction

D.Z. Lantzouraki[1], V.J. Sinanoglou[2], M. Goliomytis[3], M. Charismiadou[3], S.G. Deligeorgis[3] and P. Zoumpoulakis[4]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis 15771, Athens, Greece
[2]Instrumental Food Analysis Laboratory. Department of Food Technology. Technological Educational Institution of Athens. Ag. Spyridonos 12210 Egaleo, Greece.
[3]Department of Animal Breeding and Husbandry, Faculty of Animal Science and Aquaculture, Agricultural University of Athens, Greece
[4]Institute of Biology, Medicinal Chemistry and Biothechnology, National Hellenic Research Foundation. 48 Vas. Constantinou Ave. 11635, Athens, Greece

E-mail: dlantzouraki@gmail.com

P1-15

Studies based on diets enriched in natural antioxidants in order to improve the quality of food of animal origins, have been widely conducted. The egg and especially egg yolk is considered a functional food as it is a rich source of protein, vitamins and lipids, such as phospholipids, polyunsaturated fatty acids and carotenoids. The fatty acid profile of poultry egg yolk may be affected, among others, by diet, age of hen and geographic location. Egg yolk fatty acid profile is directly linked to the fatty acid profile of diets.

Under this approach, the effect of feed supplementation with natural antioxidants on the fatty acid composition of egg yolk lipid fractions was studied. A total of 72 laying hens, were randomly distributed into six dietary treatments and the experiment was conducted over a period of nine weeks. Hesperidin (0.75 and 1.50 g / kg of control diet), naringin (0.75 and 1.50 g / kg of control diet) and vitamin E (0.20 g / kg of control diet) were used, separately, in the diets of the five treatment groups, respectively. Feed and water were provided ad libitum. Eggs were collected at week 0, 1, 5 and 9 and their yolks were used for total lipid, fatty acid and color analyses. Fatty acid profile of egg yolk lipids was similar in all treatments. Contradictory to the above results, fatty acid proportions were significantly affected by the duration of feed. Therefore, polyunsaturated fatty acids, mainly linoleic acid, were significantly decreased, especially after five weeks of feeding. Saturated fatty acid proportion significantly varied during the experiment, whereas monounsaturated fatty acid proportion showed a significant increase, especially after five weeks of feeding. The n-6/n-3 fatty acid ratio increased significantly only in the first week of diet. The egg yolk color, which is an important parameter for consumer acceptance, depends on the levels, the type and the ratio of pigmenting substances, namely, xanthophylls, present in the hens' feed. Egg yolk color was most affected by the experimental duration rather than feed supplementation. Furthermore, yolk chroma (C) shifted from yellow to a more intense red color after 1 week of the experiment, whereas hue (h) value significantly decreased.

Acknowledgments: This work is supported from the Programme THALIS 2012-2015, SECTORAL OPERATIONAL PROGRAMME, EDUCATION AND LIFELONG LEARNING –ESPA 2007-2013.

Detection of aflatoxin M_1 in traditional local cheeses of Greece with a direct competitive ELISA

A. Batrinou[1], Ch. Kapsali[1], I. Karachristou[1], K. Tampratzi[1], D.Z. Lantzouraki[2]

[1]Laboratory of Food Microbiology, Food Technology Department, Technological Educational Institution of Athens, Egaleo, Athens, Greece
[2]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis 15771, Athens, Greece

P1-16

E-mail: d.lantzouraki@chem.uoa.gr

The aflatoxins are a group of toxic secondary metabolites known to be human carcinogens based on sufficient evidence of carcinogenicity from studies in humans. Aflatoxins are produced from fungi of the genus *Aspergillus* (mainly *Aspergillus flavus* and *Aspergillus parasiticus*) that contaminate different agricultural commodities. Aflatoxin M_1 (AFM_1) is a major metabolic hydroxylation product of Aflatoxin B_1 (AFB_1) which is the most toxic aflatoxin. AFM_1 is formed in the liver and excreted into the milk of lactating animals following ingestion of feed contaminated with AFB_1. As a consequent, dairy products such as cheese, destined for human consumption are often contaminated with AFM_1. Considering the risk of exposure of the general population to aflatoxins, maximum levels of aflatoxins (aflatoxins B_1, B_2, G_1, G_2 and M_1) in foods and feed are established in Commission Regulation (EC) No 1881/2006 as amended by Commission Regulation (EU) No 165/2010. A limit of 50 ng/kg of AFM1 for milk and 25 ng/kg for baby milk food was set. In addition, regulatory limits for dairy products, such as cheese, have been also introduced by some European countries: Netherlands (200 ng/kg), Austria and Switzerland (250 ng/kg) and Italy (provisional limit of 450 ng/kg). In this pilot study, 7 traditional local varieties of cheese from the Aegean area (Andros island) were analyzed with a quantitative direct competitive enzyme-linked immunosorbent assay (Veratox® for AFM_1provided by Neogen, a kit validated for quantification of AFM_1 in liquid raw milk and cheese with LOQ=5ppt). Most of these cheeses are produced from raw or slightly thermized ewes' or goats' milk, without the addition of commercial starters but by using only the natural microbiota of the milk. These cheeses have various local names like Kopanisti, Volaki, Armeksia etc. and their ripening period ranged from 1 month to 8 years. The results showed that 2 out of the 7 cheeses analyzed were contaminated with AFM1 at levels 174.73 and 113.85 ng/Kg, which were below the recommended maximum allowable levels of most European countries. Both contaminated cheeses had a low ripening period (1 month). Further studies should be conducted to obtain a clear picture of the AFM1 contamination in cheese in Greece, since it varies according to the initial AFM1 levels in milk, the cheese type and the technologies applied.

References

[1] L. Cavallarin et al., *Food Control*, 38 (2014) 174-177.
[2] S.Virdis et al., *Food Control*, 19 (2008) 44–49.

Evaluation of the fatty acid profile in donkey's milk during lactation

Th. Massouras and G. Alexiou

Department of Food Science and Human Nutrition, Laboratory of Dairy Science and Technology, Agricultural University of Athens, Iera odos 75, 11855 Athens, Greece

E-mail: theomas@aua.gr

P1-17

There is increasing interest in using donkey's milk for human nutrition, due to its high nutritional value and the presence of antimicrobial compounds. In this work, the fatty acids composition of donkey's milk and its variations during lactation, were investigated. Individual milk samples were collected from 3 different donkey Greek farms 30, 60, 90, 120, 180, 210 and 270 days after foaling. The fat, protein and lactose contents were determined using an infrared milk analyser (Milkoscan 6000), and fatty acids composition by gas chromatography. The results showed that donkey's milk was characterized by low fat and proteins content. The fatty acids patterns were influenced by the lactation stage, and showed a decrease in SFA content and an increase in UFA content. The SFA content in the milk decreased significantly ($P < 0.01$) during the lactation period (−36.9%). Among the SFA, palmitic acid was observed to be the most concentrated (C16:0=19.68% average). Lower average concentration levels were observed for caprylic (C8:0=4.01%), capric (C10:0 = 8.77%), lauric (C12:0 =7.90%), myristic (C14:0=4.86%), with the lowest level observed for stearic acid (C18:0=0.84%).
The overall unsaturated fatty acid (UFA) content of the milk was 53.35 ± 2.27% and increased during the lactation period. The mean UFA/SFA ratio was 1.2, which underwent a significant increase over time, reaching a value greater than 1.77% at day 270. The overall MUFA content was 31.00 ± 0.77%. The stage of lactation affected the MUFA content. The total MUFA increased ($P<0.01$) during lactation from 29.19% at day 30 to 39.36% at day 270. Oleic acid (C18:1 n-9) was the most representative of MUFA (25.07%, average), with a significant increase reaching a maximum level at day 270 (30.34%). The average palmitoleic acid (C16:1) content was 4.09%.

Composition, aromatic profile and coagulation properties of milk of goat graze in pasture of Algerian semi-arid areas.

A. Bouguerra[1], S. Djebili[1], M. Barkat[1] and Th. Massouras[2]

[1]BIOQUAL laboratory, Department of biotechnology, I.N.A.T.A.A, Mentouri Brother's Univerity. Ain El Bey, 25000 Constantine, Algeria
[2]Department of Food Science and Human Nutrition, Laboratory of Dairy Science and Technology, Agricultural University of Athens, Iera odos 75, 11855 Athens, Greece

E-mail: theomas@aua.gr

P1-18

The Algerian semi-arid areas have a great diversity of aromatic plants and the farming of goats by the population of these areas is very popular. According to an investigation realized by Bouguerra et al. [1] in the semi-arid area of east Algeria, several of medicinal herbs can easily be detected in goat milk flavour. In this context, the objective of this study was to characterize the chemical composition, coagulation properties and volatile compounds of milk from goat graze in pasture of Algerian semi-arid areas. The goat's milk samples were collected from 21 farmers. The milk composition (fat, total protein, lactose, and total solids) of the bulk tank milk samples were determined using a CombiFoss6000 FC apparatus (Foss Electric A/S, Hillerød, Denmark). Formagraph instrument was used for the measurement of coagulation parameters: clotting time (r), curd firming rate (K20) and curd firmness (A30). The Volatile compounds (VC) content in milk was identified by headspace solid-phase microextraction (HS-SPME) coupled to gas chromatography/Mass Spectrometry (GC/MS). These results obtained from this experiment indicated that the mean values of gross chemical- composition of milk varied significantly during lactation period, with high values in the early and the late lactations respectively. These values were ranged as follows : fat 3,10-7,72% (w/w), protein 3,20-4,30% (w/w), lactose 3,74-4,91% total solids 11,1-16,75% (w/w). None significant variations were observed for the coagulation parameters considered the different regions tested. About 70 volatile compounds were isolated and identified from GC-MS analysis including: aldehydes, ketones, alcohols, esters, organic acid, hydrocarbons, furans and sulphur compounds. The flavour variability observed in goat milk is linked with the aromatic plants of Algerian semi-arid areas. This work provides information on the current physicochemical, aromatic profile and technological characteristics of milk of goat graze in pasture of Algerian semi-arid areas, which can be of great importance in the dairy sector.

References

[1] A. Bouguerra, M. Barkat, N. Zouaoui et N. Diab. Séminaire International sur les Sciences Alimentaires, Constantine 14-16 octobre 2014, Algérie.

Chemometrical development and comprehensive validation of a SPME/DI-GC-MS method for the determination of 21 important free and glycosidically bound aromatic compounds in wines. Application in Greek and international *Vitis vinifera* varieties

M. Metafa[1],Th. Varzakas[3], A. Vlyssides[4], C. Israilides[1] and A. Economou[2]

[1]Institute of Technology of Agricultural Products (ITAP), Hellenic Organization 'DEMETER" (ELGO-DEMETER), 1 S. Venizelou Street, Lycovryssi, Athens 141 23, Greece
[2]Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Athens 157 71, Greece
[3]TEI Peloponnese, Dept. of Food Technology
[4]Technical University of Athens, School of Chemical Engineering

E-mail: mmetafa@nagref.gr

P1-19

In this work, a solid-phase microextraction/gas chromatography–mass spectrometry (SPME/GC–MS) methodology was developed for the determination of 21 free and glycosidically-bound volatile varietal aroma compounds in wines. Initially, a comparison was made of 5 commercially available SPME fibers for the isolation/preconcentration of the target compounds in the headspace (HS) and direct immersion (DI) modes. The statistical significance of the microextraction variables was evaluated using a 2-level Plackett–Burman experimental design; the most significant variables were further optimized using a modified Simplex procedure. Using the selected conditions, a GC–MS method was fully validated for the quantitative determination of the 21 free primary aroma compounds. The hydrophilic bound precursors were isolated by solid-phase extraction (SPE) [1], enzymatically hydrolyzed to liberate them as the free compounds and further detected by SPME/GC–MS. The method has been successfully applied to the analysis of 20 Greek white wine samples as shown in Fig 1.

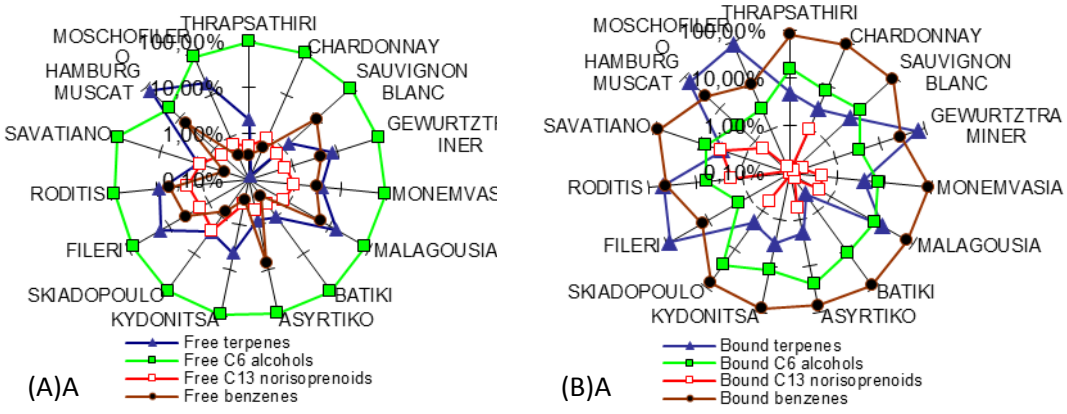


Fig 1.: Distribution (%, in logarithmic scale) of the volatile compounds in the 11 Greek and 4 international varieties: (A) in the free fraction (not including b-phenylethanol), and (B) in the bound fraction.

References

[1] M. Metafa and A. Economou, *Central European Journal of Chemistry*, 11 (2013) 228-244.

Analytical challenges in investigating allergenic proteins in varieties of *Solanum lycopersicum*

R.T. Mócsai[1], A. Maczó[1], K. Majer-Baranyi[1], N. Adányi[1], P. Milotay[2], Zs. Bánfalvi[3] and R. Tömösközi-Farkas[1]

[1]Food Science Research Institute, National Agricultural Research and Innovation Centre
H-1022 Budapest, Herman Ottó str. 15.
[2]Vegetable Crop Research Department, National Agricultural Research and Innovation Centre
H-6000 Kecskemét, Mészöly Gyula str. 6.
[3]Agricultural Biotechnology Institute, National Agricultural Research and Innovation Centre
H-2100 Gödöllő, Szent-Györgyi Albert str. 4.

E-mail: r.mocsai@cfri.hu

P1-20

In present, breeding of plants must take into account not only the specific needs of horticulture, but also the consumers' expectations. Climate change poses a new challenge to the realization of agro-technical requirements, while the quality of crops and their nutritional value also need to be paid attention to. Traditional plant breeding uses wild and related species as a source of genes. Along with the resistance genes, other chromosome regions coding potentially toxic metabolites or allergenic proteins can be transferred to the new varieties. The determination of allergenic proteins is an important task, especially in the case of tomatoes, which are usually eaten fresh without any heat treatment. The estimation of allergy to tomato is about 0.3 % worldwide, and may cause serious health risks for susceptible individuals. Several tomato allergens' sequence show homology with other allergens' sequences thus arises the possibility of cross-reactivity.

We examined varieties often used for Hungarian horticulture. Protein extracts were prepared from the different tissues of the fruit (pericarpium, mesocarpium, granum) and the soluble protein content was determined by fluorometry. The extracts were analysed by SDS-PAGE, where protein bands were identified in the molecular weight region of well-known tomato allergens, like *Lyc e 2*, *Lyc e 3*, PG2A, *etc*. A 50 kDa granum protein was isolated on a FPLC anion exchange column and the immunoactivity was examined by immunoblotting using tomato allergic human sera. We recognised non-specific binding of the secondary antibody (goat antihuman IgE), therefore conducted deglycosylation [1] and Schiff staining [2]. The antibody-antigen binding was checked by OWLS based immunosensor.

Our long term goal is selecting varieties which can be used on the basis of optimal metabolite composition for safe and healthy fresh market consumption, possibly production of hypoallergenic fresh vegetables as well as ingredients for baby food. Based on our results, it can be stated that the continuation of a series of experiments is of great importance both by agricultural and nutritional scientific perspectives.

The research is supported by the Hungarian Ministry of Agriculture.

References

[1] M.P. Woodward, W.W. Young and R.A. Bloodgood, *J Immunol Methods*, 78 (1984) 143-153.
[2] R.M. Zacharius, T.E. Zel, J.H. Morrison and J.J. Woodlock *Anal Biochem*, 30 (1969) 148-152.

Examination of bioactive components and properties of aroma in paprika powders

H. Molnár[1], M. Pék[2], R. Farkas Tömösköziné[1] and N. Adányi[1]

[1] Food Science Research Institute, National Agricultural Research and Innovation Centre, Budapest, Herman Ottó str. 15. H-1022
[2] Vegetable Crop Research Department National Agricultural Research and Innovation Centre), Obermayer square 9, 6300 Kalocsa

E-mail: h.molnar@cfri.hu

P1-21

Paprika powders produced in Kalocsa included in the register of geographical indications and protected designation of origin, thereby they are protected against the abuse of the use of the name.
The measurements were carried out from five new varieties paprika powders (paprika powders with stem and without stem) from Kalocsa, and from foreign paprika powders (Spanish, Peruvian, Chinese, Brazilian), examining the effect of the post-ripening and storage. During our investigations we determined and compared the bioactive components and aroma properties that affect the quality of the paprika. Components peculiar to the colour and the quality of the paprika and analysis of groups of compounds were performed. The amount of carotenoids, tocopherols, flavonoids and ascorbic acid were determined by HPLC and the flavouring properties by GC-MS. The determination of ASTA colour value was performed according to MSZ 9681-5:2002 requirements.
In paprika the ratio of the red compounds is higher than the yellow ones. The ASTA colour value were higher in case of paprika powders without stem than with stem, but in terms of foreign paprika the Chinese ones had lower ASTA colour value than Hungarian ones. Considering the tocopherol and ascorbic acid values the same tendency can be observed. After paprika ripening we obtain a product with these features: favourable pigment composition and high colouring capacity. Our measurements show that the amount of carotenoids and tocopherols significantly increased in case of the post-ripened paprika powders. There is no clear tendency considering the changes in the concentration of ascorbic acid. The concentration of total tocopherol and ascorbic acid were greater in the Hungarian samples than in the Chinese paprika. The total tocopherol content of the Brazilian paprika was outstanding. The most important organoleptic properties of the paprika is the aroma. Knowing the volatile material composition of the paprika we may have the opportunity to identify the variety. In case of paprika powders without stem we detected more aroma components than with stem. The amount of certain components reduce (acetic acid) and increase (β-elemen). During the analysis of aroma components significant differences were found between the different varieties of paprika.

Acknowledgments: *This research was executed in the framework of the EU-project SPICED (Grant Agreement: 312631) with the financial support from the 7th Framework Programme of the European Union. This publication reflects the views only of the authors, and the European Commission cannot be held responsible for any use which may be made of the information contained therein.*

SERS and 2D-Fluorescence for the investigation of aminoacids and egg proteins

A. Philippidis[1], Z.E. Papliaka[1] and D. Anglos[1,2]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1385, GR-711 10 Heraklion, Crete, Greece
[2] Department of Chemistry, University of Crete, P.O. Box 2208, GR 71003 Heraklion, Crete, Greece

E-mail: filagg@iesl.forth.gr

P1-22

Surface-Enhanced Raman Spectroscopy (SERS), is a powerful spectroscopic technique in the field of organic and biological materials analysis. SERS has found application in identification of organic pigments and dyes in works of art [1]. Fluorescence spectroscopy, in addition, has been used in the field of conservation of art works for the characterization of pigments and proteinaceous binding media [2].
A compact mobile Raman spectrometer is employed for collecting SERS spectra from natural aminoacids (L-Trp, L-Tyr, L-Cys) and protein films (e.g. egg white). The investigation and constant search of the appropriate substrate (Ag and/or Au nanoparticles) and methodology for performing SERS measurements is crucial for further application in analysis of organic and bio-organic archaeological residue materials. In this work we extend the first attempt of adapting a mobile Raman instrument to the SERS analysis of simple organic molecules as aminoacids and oligo- peptides [3].
The 2D-fluorescence spectroscopy (excitation-emission) technique was used in a complementary manner in the investigation of samples that are mixtures of different molecules, as proteins, revealing the presence of different fluorophores in the sample. Dry film of egg proteins were investigated following environmental and artificial ageing. The different content of specific aminoacids may also determine processes that lead to protein degradation against ageing. The differentiation achieved by recording 2D-fluorescence maps is quite useful for understanding the chemical process that may have taken place in historical samples of binding media.

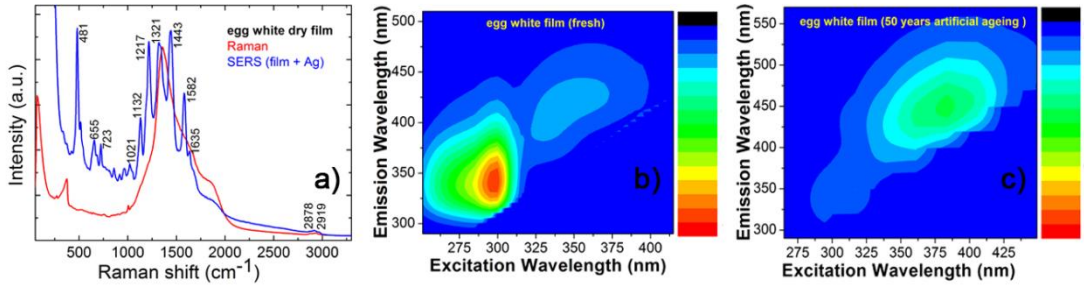


Fig. 1: Spectra collected from egg white: a) SERS, b) EE map for fresh and c) artificially aged films.

References

[1] K. Chen, M. Leona and T.V-Dinh, *Sensor Review*, 27 (2007) 109-120.
[2] A. Nevin, D. Anglos, S. Cather and A. Burnstock, *Appl. Phys. A*, 92 (2008) 69-76.
[3] A. Brambilla, A. Philippidis, A. Nevin, D. Comelli, G. Valentini and D. Anglos, *J. Molec. Structure*, 1044 (2013) 121-127.

A novel dispersive liquid-liquid microextraction gas chromatography-mass spectrometry method for the determination of selected biogenic amines in wine

J. Płotka-Wasylka and J. Namieśnik

Gdańsk University of Technology, Faculty of Chemistry, Department of Analytical Chemistry, ul. G. Narutowicza 11/12, 80-233 Gdańsk

E-mail: plotkajustyna@gmail.com

P1-23

Despite the lack of official documents implementing the mandatory of determination of BA in wine, there are a number of import requirements in the EU that set limits on the concentrations of individual BA in wine. It can be assumed that it is only a matter of time before the official introduction of the regulations implementing mandatory monitoring of BAs content in the wine, including products manufactured at home and placed on the market, especially in the context of the development of regional products. Therefore, the development of new analytical methods that in a fast, cheap and safe way for the environment can be used for the qualitative and quantitative determination of each of biogenic amines in wine is essential.
A novel dispersive liquid-liquid microextraction gas chromatography mass-spectrometry method was developed for the determination of selected biogenic amines in wines. The method features the simultaneous extraction/derivatization of the amines providing a simple and fast mode of extract enrichment. The proposed method showed good linearity (correlation coefficients > 0.997), good recoveries (from 79 to 108 %). Moreover, detection limits were never over 3.2 mg /L. The developed method was successfully applied to the analysis of 15 wine samples. Several of biogenic amines analyzed were found in most of the wines, with predominance of putrescine, tyramine,, histamine, methylamine, and cadaverine.

Acknowledgments: The research is funded by the Polish Ministry of Science and Higher Education within the "Iuventus Plus" program in years 2015-2017, project no: IP2014 037573. The project is co-financed by the European Union within the European Social Fund – Human Capital Operational Programme (POKL04.03.00-00-238/12).

Microextraction in conjuction with the derivatization–strategies for the determination of BAs in wines by chromatographic techniques

J. Płotka-Wasylka and J. Namieśnik

Gdańsk University of Technology, Faculty of Chemistry, Department of Analytical Chemistry, ul. G. Narutowicza 11/12, 80-233 Gdańsk

E-mail: plotkajustyna@gmail.com

P1-24

Biogenic amines (BAs) are naturally present in wine. Histamine, tyramine and putrescine, cadaverine are the BAs found at the highest concentrations. Their detection is must and its detection in wines is well documented in the literature [1].
This work revises the derivatization approaches for the determination of BAs in wines. Different analytical techniques have been developed to determine BAs in wine, these include GC [2], LC [3], or CE [4]. The determination of BAs in wine is very difficult because they are usually present at low concentrations. Moreover, they absorb at low wavelengths, a region where numerous interfering substances are present. In addition, many ABs do not possess such properties that allow their determination using the appropriate techniques coupled with specific detectors. These problems have been solved by using a derivatization process.
Because the derivatization process is often an essential element of the whole analytical procedure, it should be important to focus on this issue and conduct a series of experiments in order to develop the most favorable conditions for the chemical conversion process of analytes. In the literature, it can be found that miniaturization and automation are key elements that should be taken into account during optimization of "green" analytical procedure, in which there is a step derivatization of analytes. The result of this approach is to reduce the waste of reagents and thus reduce the amount of waste generated. Application of microextraction techniques in conjunction with the derivatization perfectly meets the specified requirements.

Acknowledgments: The research is funded by the Polish Ministry of Science and Higher Education within the "Iuventus Plus" program in years 2015-2017, project no: IP2014 037573. The project is co-financed by the European Union within the European Social Fund – Human Capital Operational Programme (POKL04.03.00-00-238/12).

References

[1] L. Beneduce, A. Romano, V. Capozzi, P. Lucas, L. Barnavon, B. Bach, P. Vuchot, F. Grieco and G. Spano, *Ann. Microbiol.*, 60 (2010) 573.
[2] K.-J. Huang, C.-Y. Wei, W.-L. Liu, W.-Z. Xie, J.-F. Zhang and W. Wang, *J. Chromatogr. A*, 1216 (2009) 6636.
[3] L. Pan, J.M. Chong and J. Pawliszyn, *J. Chromatogr. A*, 773 (1997) 249.
[4] J.O. Fernandes and M.A. Ferreira, *J. Chromatogr. A*, 886 (2000) 183.

Studies on the synthesis of high added value products from *Nannochloropsis oceanica* using chromatographic and mass spectrometry techniques

M.G. Savvidou[1a], Th.V. Lymperopoulou[1b], K.P. Balta-Brouma[1b], M. Michailidou, K.G. Magoulas[1c], F.N. Kolisis[1a]

[1] National Technical University of Athens, School of Chemical Engineering, Athens, Greece
[a] Biotechnology Laboratory
[b] Environment and Quality of Life Center
[c] Thermodynamics and Transport Phenomena Laboratory

E-mail: kolisis@chemeng.ntua.gr

P1-25

Many marine microalgae present a promising source of omega-3 fatty acids, such as eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) as well as other chemical compounds such as astaxanthin used in several biological applications related with health benefits, antimicrobial and antioxidant activity. The marine microalga *Nannochloropsis oceanica* (strain CCMP1779) is an important source for omega-3 fatty acids and a potential candidate for pigment production (astaxanthin).The aim of this research was to investigate the possible relationship between the medium composition and the distribution pattern of fatty acids in order to define the parameters favoring the production of long chain unsaturated acids. Furthermore, the enzymatic synthesis of astaxanthin esters was examined. Astaxanthin, an effective antioxidant, protects the skin from radiation injury due to sunlight, decelerates age related and improves the immune system, while its esters which show better oral-absorbability are expected to add value to this natural product. The growth rate of *Nannochloropsis oceanica*, the total lipid content and the overall profile of free fatty acids as well as the astaxanthin esters were extensively studied. The lipid extract was qualitatively analyzed using GC-MS technique and all samples were esterified prior to the analysis in order to be determined in the form of the more volatile methyl-esters. Free astaxanthin as well as its esters were identified and measured using APCI LC-MS technique.

References

[1] Guedes C, Amaro H, Barbosa C, Pereira R, Malcata FX. Fatty acid composition of several wild microalgae and cyanobacteria, with a focus on eicosapentaenoic, docosahexaenoic and α-linolenic acids for eventual dietary uses. Food Research International 44 (2011) 2721-2729.
[2] Kail BW, Link DD, Morreale BD. Determination of Free Fatty Acids and Triglycerides by gas Chromatography Using Selective Esterification Reactions. Journal of Chromatographic science (2014) 00:1-6

Effect of gamma radiation on the fatty acid profiles of sesame oil

D. Lantzouraki[1], P. Zoumpoulakis[2], I.F. Strati[3], G.-N. Nikolaou[3], S.M. Bratakos[3] and V.J. Sinanoglou[3]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis 15771, Athens, Greece
[2]Laboratory of Molecular Analysis. Institute of Biology, Medicinal Chemistry and Biothechnology, National Hellenic Research Foundation. 48 Vas. Constantinou Ave. 11635, Athens, Greece
[3]Instrumental Food Analysis Laboratory. Department of Food Technology. Technological Educational Institution of Athens. Ag. Spyridonos 12210 Egaleo. Greece.

P1-26

E-mail: v_sinanoglou@yahoo.gr, vsina@teiath.gr

Sesame (*Sesamum indicum* L.) is one of the most important oilseed crops worldwide, and has been cultivated in Korea since ancient times for use as a traditional health food. Sesame oil is increasingly consumed due to its beneficial effects on human health. It contains constituents which act as antioxidants, lower platelet aggregation, prevent atherosclerosis and reduce serum cholesterol [1]. In this study, the effect of γ-irradiation on the fatty acid profile of sesame oil was investigated at 5.0 and 10.0 kGy doses, by GC-FID analysis. Fatty acid profile alterations after food irradiation are considered to be critical for the choice of irradiation as food preservation method. Results revealed a strong trend toward an increase in the saturated fatty acids (SFA) proportion and a decrease in the monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) proportion of the irradiated samples compared to the non-irradiated, with the increase of irradiation dose. Moreover, MUFA/SFA and PUFA/SFA ratios decreased ($P<0.05$) compared to control samples. It is important to point out that the decrease of linoleic acid (C18:2ω-6) was accompanied by an significant increase in rumenic acid (*cis*9,*trans*11-CLA) formation. Gamma irradiation induced stearic acid formation and a simultaneous oleic acid proportion decrease, in a dose dependent way. Furthermore, regarding the main unsaturated fatty acids (UFA) of sesame oil, the C18:1ω-9/C18:2ω-6 ratio was slightly reduced by irradiation process. The observed changes in the fatty acid profile were also confirmed by gas chromatography-mass spectrometry analysis of the samples.

Keywords: GC-FID; γ-irradiation; sesame oil; fatty acid profile.

Acknowledgments: This work is supported by the Programme ARHIMIDES 2012–2015, Sectoral Operational Programme, Education and Lifelong Learning — ESPA 2007–2013.

References

[1] A. Rohman, A. Martsasi and S. Riyanto, *International Food Research Journal* 20 (2013) 357-361.

Characterization of visceral oils from conventional and organically farmed *Sparus aurata*, *Dicentrarchus labrax* and *Diplodus puntazzo*

V.J. Sinanoglou, D.P. Houhoula, V.R. Kyrana and V.P. Lougovois

Department of Food Technology, Technological Educational Institution (T.E.I.) of Athens
Agiou Spyridonos 12210 Egaleo, Greece

P1-27

Crude oils recovered from the viscera of conventional and organically farmed *S. aurata*, *D. puntazzo* and *D. labrax* were characterised. Triacylglycerols (TAG) and phospholipids (PL) were the major lipid classes. Visceral oils contained high levels of omega-3 polyunsaturated fatty acids (PUFA), in particular docosahexaenoic acid (DHA) and eicosapentaenoic acid (EPA). The DHA/EPA ratios (1.66-2.46) were higher in organically farmed fish. Total PUFA and omega-3 fatty acid levels were affected both by species and rearing system, being higher in conventionally farmed sparids. The *n*-3/*n*-6 ratio (1.42-2.19) was comparable to the values reported for muscle lipids, while the PUFA/SFA ratio (1.07-1.33) exceeded the recommended value. Visceral oils exhibited good oxidative stability during storage at 63ºC. The data indicate that the viscera of all three species provide a good source for the production of omega-3 rich oils.

Material and methods. Visceral lipids from conventional and organic fish were extracted by chloroform/methanol. Lipid classes were separated by TLC-FID and fatty acid methyl esters quantified by GC-FID analysis (Sinanoglou et al., 2013). Lipid oxidative stability was evaluated by determining free fatty acids (FFA), peroxide values (PV), conjugated dienes (CD) and 2-thiobarbituric acid reactive substances (TBA-RS), over a period of four weeks (AOCS, 2005).

Results and discussion. Lipid yields varied considerably (26.53-42.61%) and were higher ($p < 0.05$) in conventional *D. labrax* and *S. aurata*. Neutral lipids comprised the major lipid class (85.3-89.4% of the TL), followed by PL (9.6-13.3%). MUFA were predominant in all three species (42.25-48.35%), followed by PUFA (26.68-32.97%) and SFA (24.76-25.79%). Omega-3 PUFA accounted for 15.69-22.65% of the total FA content and were affected both by species and rearing system. The major omega-3 FA were DHA and EPA, but α-linolenic, docosapentaenoic and steriadonic were also present in notable amounts. Linoleic acid, the principal *n*-6 PUFA, was found in significantly ($p < 0.05$) higher proportions in conventional *D. labrax* (9.95%) and *S. aurata* (9.77%). The *n*-3/*n*-6 PUFA ratio (1.42-2.19) was higher than the recommended 1:4 to 1:1 ratio. Visceral oils also displayed high PUFA/SFA ratios (1.07-1.33). During storage at 63ºC they exhibited good oxidative stability (low levels of CD, PV, TBA-RS, FFA). According to the results, visceral oils from farmed *S. aurata*, *D. puntazzo* and *D. labrax* provide a valuable source for the production of high quality marine lipids for the food and pharmaceutical industries.

References

[1] AOCS (2005). Official Methods and Recommended Practices of the American Oil Chemists' Society. Champaign, USA: AOCS Press.

[2] V.J. Sinanoglou, C. Proestos, D.Z. Lantzouraki, A.C. Calokerinos and S. Miniadis - Meimaroglou, *European Journal of Lipid Science and Technology*, *116* (2013) 134–143.

Seasonal variations in the lipid and fatty acid profiles of the smooth clam *Callista chione*

C. Papaioannou[1], V.P. Lougovois[2], V.R. Kyrana[2], I.F. Strati[1] and V.J. Sinanoglou[1]

[1] Instrumental Food Analysis Laboratory. Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos 12210 Egaleo, Greece
[2] Fisheries Laboratory. Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos 12210 Egaleo, Greece

P1-28

E-mail: v_sinanoglou@yahoo.gr, vsina@teiath.gr

This study was conducted with a view to identifying seasonal variations in the lipid content of smooth clam *Callista chione*, focusing on the individual lipid classes and total lipid fatty acid (FA) profile. Seasonal changes in total lipids showed a characteristic pattern, with maximum accumulation in summer (2.46%) and minimum levels during autumn (0.92%). The proportion of total neutral lipid (NL) was significantly higher than that of polar lipids (PL) during spring and summer, though the opposite was observed during autumn. Gas chromatography revealed the presence of 40 fatty acids (FA), among which saturated fatty acids (SFA) prevailed throughout the year, followed by polyunsaturated (PUFA) and monounsaturated (MUFA) fatty acids. Total PUFA reached the highest levels in autumn. Palmitic acid (C16:0) was the most abundant fatty acid at all–seasons, ranging from 24.34 to 25.82%. Docosahexanoic (DHA, C22:6ω-3) and eicosapentanoic (EPA, C20:5ω-3) acids were found to be predominant among PUFAs. The seasonal change primarily affected stearic (C18:0), oleic (C18:1ω-9), linoleic (C18:2ω-6) and DHA (C22:6ω-3), with higher proportions found during autumn, and myristic (C14:0), palmitoleic (C16:1) and EPA (C20:5ω-3), which were more abundant during spring. The highest ω-3/ω-6 ratios were observed in spring and summer. Concerning lipid quality indices, seasonal change mostly affected hypocholesterolaemic and peroxidisability indices, with higher values found during autumn and atherogenic and hypercholesterolaemic indices displaying higher values during spring. As a conclusion, significant variations in FA profiles were observed with season, possibly related to the spawning cycle of the bivalve and the plankton blooms triggered by sea water temperature.

Analysis and classification of ham meat products according to meat type and processing, using colour and texture analysis methods

D. Xenogiannopoulos[1], G. Xenogiannopoulos[2], P. Zoumpoulakis[3], D. Cavouras[2] and V.J. Sinanoglou[1]

[1]Instrumental Food Analysis Laboratory, Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos Street, Aigaleo GR-12210, Athens, Greece.
[2]Medical Image and Signal Processing Laboratory, Department of Biomedical Engineering, Technological Education Institution of Athens, Ag. Spyridonos Street, Aigaleo GR-12210, Athens, Greece.
[3]Institute of Biology, Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, 48, Vas. Constantinou Ave., 11635, Athens, Greece.

E-mail: v_sinanoglou@yahoo.gr, vsina@teiath.gr

In this study statistical procedures were employed to characterize and classify commercial ham slices in terms of meat type and processing. Two types of commercial hams (made from pork and turkey) and two types of processing (boiled and smoked) were used. Hams were sliced, and from each slice, a number of features were calculated, related to texture and colour. From each slice, textural features computed from the slice's digital image, and colour features measured by a chromatometer, were extracted. Principal component analysis (PCA) was applied in order to highlight an initial grouping of the samples, depending on meat type and processing, and to gain suitable information for the selection of the most appropriate features for the potential separation among groups. Discriminant analysis, employing pattern recognition methods, was finally applied for classifying ham slices first into processing type groups (boiled or smoked) and next into meat origin groups (pork and turkey). The colour and image analysis could represent a fast and non-destructive classification tool among certain meat products, not requiring chemical analyses. This may be of value to food industry in predicting meat origin and treatment type of meat products.

Keywords: commercial ham; colour and texture analysis; discriminant analysis.

Determination of hydrolysed proteins' molecular weight in fish feeds using size exclusion chromatography and UV detection

G. Koulis, M. Dasenaki and N.S. Thomaidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zographou, 15771 Athens, Greece

E-mail: ntho@chem.uoa.gr

P1-30

The increasing cost of fish feeds and live preys rendered necessary to find alternative protein sources in fish's diet. Hydrolysed proteins, which derive from the hydrolysis of slaughterhouse's by-products in specific processing plants, are rapidly gaining ground over the last decades. What the legislation dictated for such products is that their molecular weight must not exceed 10,000 Da due to the fear of spreading transmissible spongiform encephalopathies. Nowadays, this limit only exists for hydrolysed proteins derived from ruminants. For the other animal by-products the legislation specifies that hydrolysed proteins must only be peptides, polypeptides and free amino acids which have proven to be beneficial for fishes' growth and health. Thus, in order to ensure fish feed quality and safety, the development of analytical methods for the control of hydrolysed proteins is completely essential. In this study, a liquid chromatographic method with UV/Vis detection for the determination of the molecular weight of hydrolysed proteins in fish feeds, was developed and optimized. For the separation of hydrolysed proteins in fractions based on their molecular weight, size exclusion chromatography was used and the subsequent determination of molecular weight was accomplished by absorbance measurements at 280 nm. The extraction of the hydrolysed proteins was performed under strong denaturing conditions (0.05 M Tris-HCl buffer adjusted at pH 8.5, 8 M urea, 0.25% SDS, 1.5 M 2-mercaptoathanol). The optimized method is linear over the whole column fractionation range (200-75,000 Da) and the % deviation between the experimental and theoretical molecular weight ranged from 3.0% (cytochrome c) to 8.4% (carbonic anhydrase). The repeatability %RSD values ranged from 3.0% (albumin) to 8.9% (aprotinin).

Novel NMR spin- chromatography method for the identification and quantification of glutathione in white wine

V.G. Kontogianni[1], C.G. Tsiafoulis[2,3], I.G. Roussis[4] and I.P. Gerothanassis[1]

[1] Section of Organic Chemistry and Biochemistry, Department of Chemistry
[2] NMR Center
[3] Laboratory of Analytical Chemistry, Department of Chemistry
[4] Laboratory of Food Chemistry, Department of Chemistry,
University of Ioannina, Ioannina GR-451 10, Greece

P1-31

Glutathione (GSH) is a tripeptide consisting of glutamate, cysteine and glycine. Upon grape crushing, GSH is extracted into the must where it exerts protective effect against oxidation (during the vinification process). During wine storage / ageing, GSH impedes the decrease of important aroma compounds, prevents the development of atypical ageing off-flavours and inhibits the browning of wine during storage / ageing. Elevated GSH levels in wine, in particular white wine which is more sensitive to oxidation, may be highly valuable for wine quality [1, 2, 3].
A novel, rapid and direct identification and quantification of GSH in fresh white wine with the use of selective 1D TOCSY NMR experiments is presented [4, 5]. The spin chromatography method does not involve derivatization and/or extensive sample preparation procedures, apart from the freeze drying of wine and the adjustment of pH. It allows the spin-coupling network to be elucidated even when the signals of GSH are not recognized in the 1D ^{1}H-NMR spectrum of a spiked sample because of the presence of strongly overlapped regions of the spectra and the coexistence of major components such as glycerol with $1x10^{3}$ stronger NMR signal intensities.

References

[1] E.C. Kritzinger, F.F. Bauer and W.J. du Toit, *J. Agric. Food Chem.*, 61 (2013) 269-277.
[2] D. Papadopoulou and I. G. Roussis, *Int. J. Food Sci. Tech*., 43 (2008) 1053-1057.
[3] I. G. Roussis and S. Sergianitis, *Flavour Fragr. J.*, 23 (2008) 35-39.
[4] P. Sandusky and D. Raftery, *Anal. Chem.*, 77 (2005) 2455-2463.
[5] C. Papaemmanouil, C.G. Tsiafoulis, D. Alivertis, O. Tzamaloukas, D.Miltiadou, A. Tzakos and I.P. Gerothanassis, *J. Agric. Food Chem.* (2015), in press (DOI 10.1021/acs.jafc.5b01335).

Investigation on Greek white and red wines using optical absorption and Fluorescence spectroscopy in combination with Chemometrics

E. Poulakis[1,2], A. Philippidis[1], M. Velegrakis[1]

[1] Institute of Electronic Structure and Laser, Foundation for Research and Technology Hellas (IESL-FORTH), Heraklion, Crete, Greece
[2] Department of Chemistry, University of Crete, Heraklion, Greece

E-mail: vele@iesl.forth.gr

P1-32

Optical spectroscopic methods such as Ultraviolet/Visible/Near Infrared Absorption and Fluorescence spectroscopy, with no or minimum sample pretreatment, were applied to provide the chemical fingerprint for the exploration of Greek wines, and particularly those cultivated in the region of Crete and are considered to be typical local varieties.
Unsupervised statistical multivariate techniques such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) were used for the exploration and simpler visualization of our spectral data. A pure discrimination among varieties was observed both with absorption and fluorescence spectroscopy. The application of PCA gives the possibility to correlate the absorption spectra with the chemical composition of the wines, allowing thus comparisons among different varieties.
Discriminations among barrels and ageing time in some cases were also observed. Finally, multivariate calibration methods such as Partial Least Squares (PLS) regression were used in order to investigate the ability of the spectroscopic methods in predicting some qualitative and quantitative characteristics of the wines such as alcohol index, chemical compounds' concentration, phenolic index, mixture content and sensory characteristics.

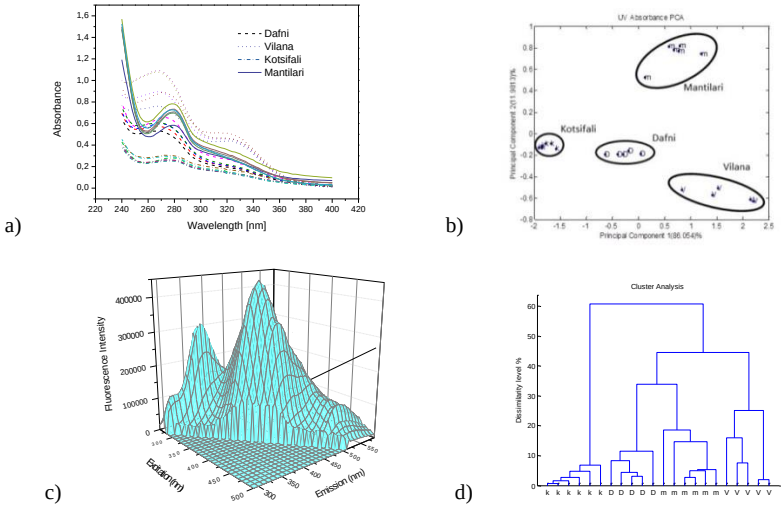


Fig. 1: a) Absorption spectra of 22 different wine samples b) Discrimination of varieties with PCA c) Emission Excitation Matrix (EEM) d) Discrimination of varieties with HCA

Determination of quinolones in fish muscle plus skin by ultra high-performance liquid chromatography with photo–diode array detection

V. Zonaras and Y. Kotzamanis

Hellenic Center for Marine Research, Institute of Marine Biology, Biotechnology and Aquaculture, Agios Kosmas 16604, Hellenikon (Greece)

*E-mail: vzonaras@hcmr.gr

P1-33

Quinolones (*QN*s) are antimicrobial drugs widely used in fish farming for prophylactic and therapeutic purposes. During the last decades, they have received growing attention for their potential in fish therapy against various systemic bacterial infections. However, the potential hazards associated with their residues in the edible tissues of farmed fish include allergies, toxic effects and antimicrobial resistance. For this reason, European Union (*EU*) has established Maximum Residue Limits (*MRL*s) in order to limit human exposure to these drugs. Oxolinic acid and flumequine are members of the older generation of *QN*s which are less efficient but still regularly used in fish farming. Enrofloxacin, ciprofloxacin, danofloxacin and sarafloxacin are later–generation fluoroquinolones (*fQN*s). Nalidixic acid is one of the earliest–known members of the quinolone class with limited activity [1].

In this study an Ultra High Performance Liquid Chromatography and Photo Diode Array (*UHPLC-PDA*) method was developed and validated for the determination of the aforementioned *QN*s in fish muscle plus skin using enoxacin as internal standard. Tissues from the two leading species of Greek aquaculture were used: gilthead sea bream (*Sparus aurata*) and European sea bass (*Dicentrarhus labrax*). The analytes were extracted from fish tissue by acetonitrile followed by the salting out of water using anhydrous magnesium sulfate, sodium chloride and buffering citrate salts to induce liquid-liquid partitioning. Fish tissue extracts were subjected to dispersive solid phase extraction (d*SPE*) using a C_{18} sorbent and were then ready for analysis. Chromatographic analyses were performed using the *UHPLC* system model Acquity (Waters, USA) and separations were achieved on a *BEH* C_{18} 2.1×100 mm, 1.7 μm analytical column kept at 50 ^{o}C. Mobile phase was consisted of water and acetonitrile containing formic acid 0.1 % (v/v) and was pumped at a flow rate of 0.4 mL min^{-1} using a gradient elution program. *QN*s detection was achieved by a *PDA* detector monitored at 260, 275 and 280 nm and by using the Empower software (Waters, USA). The developed method was validated for fish muscle plus skin tissue according to the requirements set by the Commission Decision 2002/657/*EC* and used for the residue determination of *QN*s in farmed gilthead sea bream and sea bass purchased from local markets.

References

[1] E. Evaggelopoulou and V. Samanidou, *Food Chemistry*, 136 (2013) 479-484.

A comparative study on maternal milk's lipid composition

G.-N. Nikolaou[1], V.J. Sinanoglou[1], D.Z. Lantzouraki[1], D. Cavouras[3], Th. Boutsikou[4], D.D. Briana[4], A. Malamitsi-Puchner[4] and P. Zoumpoulakis[2]

[1]Instrumental Food Analysis Laboratory. Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos 12210 Egaleo, Greece
[2]Institute of Biology, Medicinal Chemistry and Biotechnology, National Hellenic Research Foundation, Vas.Constantinou Ave., 11636, Athens, Greece
[3]Medical Image and Signal Processing Laboratory, Department of Biomedical Engineering, Technological Education Institution of Athens, Ag. Spyridonos 12210 Egaleo, Greece
[4]Neonatal Division, 2nd Department of Obstetrics and Gynecology, Athens University Medical School, Athens, Greece

E-mail: pzoump@eie.gr

P1-34

Maternal milk from healthy women living in Greece was collected the third day postpartum, in order to investigate the potential impact of various factors on the fatty acid profile of the milk fat. Certain lipid quality indices (LQI) and fatty acid ratios were estimated and results were statistically processed.
The main identified fatty acids (FA) were palmitic (C16:0), oleic (C18:1ω-9), and linoleic (C18:2ω-6). Among FA, saturated fatty acids (SFA) predominated (39.27%), followed by monounsaturated fatty acids (MUFA) (29.47%), while polyunsaturated fatty acids (PUFA) had the lowest proportion (7.44%). Furthermore, lipid quality indices' values were found within the reported range from the literature.
Mothers' body mass index (BMI) potential influence on milk's FA profile was firstly considered. Significant differences were noted among samples concerning α-linolenic (C18:3ω-3), lauric (C12:0) and palmitic (C16:0) acids' percentages. Secondly, the effect of mothers' nationality was examined, wherein significant differences were found regarding SFA and MUFA proportions as well as the thrombogenic (TI), hypocholesterolemic (hI) and hypercholesterolemic (HI) indices. Furthermore, the potential influence of mothers' age on milk fat fatty acid profile was studied, wherein significant differences were also found. Moreover, the type of the parturition, i.e. physiological birth, caesarean or premature labor by caesarean, has been examined and significant differences were observed mainly for the proportions of myristic (C14:0) and oleic (C18:1ω-9) acids. The impact of the Fetal Weight Percentile on breast milk fatty acid profile was also studied, and significant differences were also observed.
The aforementioned findings suggest that the fatty acid profile of colostrum milk fat was mainly affected by mothers' nationality and age rather than the type of the parturition and mothers' body mass index. Therefore, circumstantial knowledge of the factors affecting fatty acid profile of maternal milk will be helpful to establish the optimal amounts and relative ratios of different fatty acids in infant diets that provide the best outcomes.

Keywords: Maternal milk; fatty acids; GC-FID analysis, lipid quality indices.

Investigation of flavonoid enriched ration on chicken plasma metabolites

Ch. Fotakis[1], P.E. Simitzis[2], M. Goliomytis[2], S.G. Deligeorgis[2] and P. Zoumpoulakis[1]

[1] Institute of Biology, Medicinal Chemistry and Biotechnology, National Hellenic Research Foundation, 48 Vas. Constantinou Ave., 11635, Athens, Greece
[2]Department of Animal Breeding and Husbandry, Faculty of Animal Science and Aquaculture, Agricultural University of Athens, Greece

E-mail: pzoump@eie.gr

P1-35

The use of flavonoids as dietary supplements is well established mainly due to their intense antioxidant and anti-inflammatory properties. In this study, two main citrus flavonoids, hesperidin and naringin, in different concentrations, were used to enrich poultry rations in order to achieve meat products of better quality.
NMR based metabolomics and CPMG pulse sequence was implemented on chicken blood plasma specimens in order to discern whether bioflavonoid enriched rations have led to certain metabolite alterations in blood.
In this direction, the spectral data was subjected to multivariate data analysis using the SIMCA 14 software. Supervised analysis (OPLS-DA) traced variations in the metabolic pattern according to the sustenance consumption which was attributed to specific metabolites with the application of the S-line plot. Particularly, samples fed with hesperidin in contrast to control ones are characterised by increased levels of di-saccharide, threonine, creatinine, carnitine, dimethylamine and glutamine/glutamate. Finally, naringin samples revealed the previous pattern when compared to control samples and in addition probed to increased levels of citrate and acetate. Results indicate that similar metabolic patterns were observed regardless the type of flavonoids incorporated in the rations. The present study verifies the scalability of NMR metabolomics to highlight metabolite variations among chicken samples in relation to the feeding ration.

Keywords: bioflavonoids; hesperidin; naringin; poultry; NMR based metabolomics

Acknowledgments: This work is supported from the Programme THALIS 2012-2015, SECTORAL OPERATIONAL PROGRAMME, EDUCATION AND LIFELONG LEARNING –ESPA 2007-2013

References

[1] Ch. Fotakis, D. Christodouleas, K. Kokkotou, M. Zervou, P. Zoumpoulakis, P.Moulos, M. Liouni and A. Calokerinos, *Food Chemistry*, 138 (2013) 1837–1846

Estimating the quality of red and white meat using chemometrics on fatty acids and lipid quality indices

V.J. Sinanoglou[1], Ch. Fotakis[2], I.F. Strati[1] and P. Zoumpoulakis[2]

[1]Instrumental Food Analysis Laboratory, Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos 12210 Egaleo, Greece.
[2]Institute of Biology, Medicinal Chemistry and Biotechnology, National Hellenic Research Foundation, Vas. Constantinou 48, Athens 11635, Greece

E-mail: vsina@teiath.gr, pzoump@eie.gr

P1-36

The aim of the present study was to evaluate, comparatively, the nutritional value of intramuscular red and white meat, in terms of its fat fatty acid profile and lipid quality indices' (LQI) values, using chemometrics. Lipids and their fatty acid constituents are important meat components and contribute to several desirable characteristics of meat and meat products. Lipids improve the tenderness and juiciness of meat and amplify it flavour and aroma profile. Lipid quality indices such as atherogenic index (AI), thrombogenic index (TI), peroxidisability index (PI), hypercholesterolaemic index (HI) and hypocholesterolaemic index (hI) cholesterol index (CI) and cholesterol-saturated fat index (CSI) as well as fatty acids ratios (MUFA/SFA, PUFA/SFA, ω-6/ω-3), summarize the positive and/or negative effect of nutritive important fatty acids in fat, as well as their atherogenic, thrombogenic, cholesterolaemic and peroxidative impact on human health. Principal Component Analysis |(PCA) was used to explore the chemometric results. PCA differentiated along the first principal component red meat (lamb and kid) from white meat (pork and chicken). In particular, chicken fat samples was mainly characterized by high PI values, while to a lesser degree followed polyunsaturated and ω-6 fatty acids, TI values and PUFA/SFA ratio. The samples of pork meat were mainly characterized by high ω-6/ω-3 and secondly h/H ratios. The red meat samples were primarily related to ω-3 fatty acids and CSI values, while to a lesser extent affected by the SFA and MUFA proportions, AI, HI and CI values and MUFA/SFA ratio. Subsequent PCA models highlighted a significant overlapping among lamb and kid samples, which suggests similarity among them. The main outcomes observed by the comparison of fatty acid profile and LQI values among red and white meat fat, were: (i) while pork and chicken meats were characterized by lower fat content and cholesterol indices (CI and CSI) than red meat, were found to have about eight times higher ω-6/ω-3 ratio; (ii) the PUFA/SFA differed significantly ($P<0.05$) among groups, whereas all values found were similar or higher to the recommended value of 0.45, which is considered as appropriate for human diet; (iii) pork meat fat although characterized by significantly lower SFA proportion compared to the other meat samples, also had the lowest peroxidisability index; and (iv) the high cholesterol indices' values of red meat fat compensated by its high ω-3 fatty acid proportion. In conclusion, discriminate analysis of several combinations of individual lipid constituents could be an effective tool to assess fat quality.

Spectrophotometric determination of flavonoids by formation of silver nanoparticles

E. Terenteva, V. Apyari, S. Dmitrienko and Yu. Zolotov

Analytical Chemistry Division, Department of Chemistry, Lomonosov Moscow State University, Leninskie gory, 1/3, Moscow 119991, Russia

E-mail: apyari@mail.ru

P1-37

Flavonoids (FLs), such as quercetin, dihydroquercetin, rutin, morin and a number of other compounds, are widely distributed in nature and play an important role in the biological processes. They were found in the medicinal herbs, fruit, vegetables, wine. As a part of pharmaceutical formulations, they are used in medicine. Control of the flavonoid contents is important to reveal drug falsification and evaluate the quality of food additives. The most important property of flavonoids is their pronounced reducing ability, which appears, for example, in the reaction of silver ion reduction to form silver nanoparticles (AgNPs).

We have studied the possibility of spectrophotometric determination of FLs based on the formation of AgNPs from silver nitrate in the presence of these compounds.

It was shown that quercetin, dihydroquercetin, rutin and morin act as reducing agents in the reaction with silver ions to form AgNPs with an intense surface plasmon resonance band at 415 nm. This fact was utilized as a basis of FL spectrophotometric determination. Effects of the nature and the concentration of a FL and a stabilizer, composition of the solution and the interaction time were studied. The maximum yield of AgNPs is achieved in the presence of polyvinylpyrrolidone (PVP) as a stabilizer under the following conditions: $c_{AgNO_3} = 2 \cdot 10^{-3}$ mol L^{-1}, c_{PVP} = 0,06 mg mL^{-1}, $c_{NaOH} = 2 \cdot 10^{-4}$ mol L^{-1}, t = 15 min.

The metrological performance of the flavonoid determination were evaluated. The limits of detection calculated by 3S-criterion are 0.03, 0.06, 0.09, and 0.1 μg mL^{-1} for quercetin, dihydroquercetin, rutin, and morin, respectively. The accuracy of the procedure developed was checked by standard addition method using model solutions. The determination of dihydroquercetin in "Dihydroquercetin" and "Kapilar" biologically active food additives was carried out to assess the possibility of practical application of the method. The results correlated well with the labeled dosage and the results obtained by an independent method – HPLC with amperometric detection. The developed method of FL determination can be used to evaluate of antioxidant activity. Evaluation of the antioxidant activity of the "Antistaks" drug was carried out. The advantages of the developed method are sensitivity, simplicity, quickness, availability of the equipment, and ease of naked-eye detection.

Acknowledgements: *The work was financially supported by the Russian Foundation for Basic Research (grant N 13-03-00100). We also thank the Center for Instruments Collective Use of Lomonosov Moscow State University and Dr. S.S. Abramchuk for recording the TEM images and ED patterns.*

Characterisation of Melanoidins and their metal complexes applying EPR and FTIR spectroscopic techniques

K. Bayer[1], M. Kaufmann[1], A. Hornemann[2], B. Beckhoff[2] and L.W. Kroh[1]

[1]Institute of Technology Berlin, Gustav-Meyer-Allee 25, 13355 Berlin, Germany
[2]Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin, Germany

E-mail: kathrin.bayer@mailbox.tu-berlin.de

P1-38

Melanoidins, brown polymeric compounds formed during the Maillard reaction, are known to be responsible for color and flavor of thermally treated food.
They can carry out both antioxidative [1] and antimicrobial [2] activities and can be used as metal scavengers for ions such as Fe^{3+} and Cu^{2+} [3]. In combination with redox-active metal ions, melanoidins may also have a pro-oxidative potential [4]. Although these properties are recorded in many publications, the responsible structural features and mechanisms are mostly unknown.
This study is intended to gain insight into different melanoidins by identifying their complexing properties and molecular structure properties applying various spectroscopic methods.
The complexing property referring to Cu^{2+} as well as the radical character of melanoidins in solid samples can be analysed by EPR (electron paramagnetic resonance) spectroscopy. The EPR results have shown that the ability of complexing Cu^{2+} decreases when melanoidins were prepared at higher temperature (440 K) while the radical character increases. Food being treated at elevated temperature loses its capability to remove redox-active metal ions of the food system and poses a higher risk by increasing radical species at the same time. The significant changes strongly depend on the respective sugar and amino acid moieties.
Structural differences among melanoidin species were attempted to be figured out by IR spectroscopic investigations. Both temperature- and concentration-dependency of IR signals in the spectral range between 1700 and 1000 wavenumbers could be observed.
In this study we will show that the analysis of Maillard model systems and the interpretation of the results can be very complex due to the diversity of melanoidins. Regarding melanoidins from real food systems, not only available sugars and amino acids but also other food ingredients can participate in the Maillard reaction mechanism, thus enlarging the potential set of end products. This is why impact on food safety and quality also with respect to health-related aspects require further profound research.

References

[1] C. Franzke and H. Iwainsky, *Deutsche Lebensmittel-Rundschau*, 50 (1954) 251-254.
[2] J. Rufián-Henares and F. Morales, *Food Research International*, 39 (2006) 33-39.
[3] T. Gomyo and M. Horikoshi, *Agr. Biol. Chem.*, 40 (1976) 33-40.
[4] B. Cämmerer, K. Chodakowski, C. Gienapp, L. Wohak, A. Hartwig and L. Kroh, *Eur. Food Res. Technol.*, 234 (2012) 663-670.

Comparison of the scavenging activity of wines, teas and edible oils determined by the CL reaction of N,N-dimethyl-biacridylidene

D.C. Christodouleas[1, 2], A. Calokerinos[1] V. Garyfali[1,2], Ch. Fotakis[1,2] and K. Papadopoulos[2]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece
[2]Division of Physical Chemistry, IAMPPNM, NCSR Demokritos, Agia Paraskevi Attikis, 15310 Athens, Greece

E-mail: calokerinos@chem.uoa.gr

P1-39

This research compares the singlet oxygen scavenging activity of several natural products (e.g., wines, teas, edible oils) determined using the N,N-dimethyl-biacridylidene /singlet oxygen CL reaction in batch and in flow conditions. The CL intensity of the reaction of N,N-dimethyl-biacridylidene with the singlet oxygen produced from hydrogen peroxide and sodium hypochlorite aqueous ethanolic solutions is directly inhibited by the antioxidants present in the sample solutions. The scavenging activity expressed in gallic acid equivalent capacity values (GEAC) of 30 natural product samples (10 wines, 10 teas and 10 edible oils) was estimated and the relative standard deviation of measurement under repeatability conditions was less than 3.0 % (N=5).

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS; Investing in Knowledge Society through the European Social Fund.

Comparison of four FIA-CL methods for the evaluation of antioxidant activity of various natural products

D.C. Christodouleas[1, 2], A. Calokerinos[1] V. Garyfali[1,2], Ch. Fotakis[1,2] and K. Papadopoulos[2]

[1]Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece
[2]Division of Physical Chemistry, IAMPPNM, NCSR Demokritos, Agia Paraskevi Attikis, 15310 Athens, Greece

E-mail: calokerinos@chem.uoa.gr

P1-40

In this study, four flow-injection chemiluminescent methods (FIA-CL), the Luminol - $KMnO_4$ system, the Lucigenin – H_2O_2 – Co^{2+} system, the $KMnO_4$ – HCHO system and the Cerium (IV) – Rhodamine B system were optimized in order to evaluate the antioxidant activity of standard compounds and various natural products. In this context, we investigated the effect of CL reagents concentration, solution pH and flow rate of the signal intensity of the developed methods. The combination of flow injection analysis with chemiluminescence detection (FIA-CL) enables fast, reproducible reagent mixing, ensures immediate transfer of the reaction zone to the CL detector and significantly reduces the time of analysis. Nine standard antioxidant compounds were measured for the evaluation of their antioxidant activity (gallic acid, caffeic acid, (±)-catechin, chlorogenic acid, ascorbic acid, vannilic acid, tyrosol, bytulhydroxy-toluene and trolox). Furthermore, the antioxidant profile of wine, beer, tea and juice was assessed. Interestingly, each antioxidant and natural product exhibited a different behavior in relation to the system under investigation.
To the best of our knowledge, no other study has previously accomplished to correlate the application of four different flow-injection chemiluminescent techniques in natural products. It is the first time that various natural products such as wine, beer, tea and fruit juice were measured by different techniques and the comparison among them shows great interest.

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS; Investing in Knowledge Society through the European Social Fund.

A chemiluminescent assay for the detection of allergens in foodstuffs

S. Christopoulou[1], D.P. Kalogianni[1], S. Karaiskou[1], P.C. Ioannou[2] and Th.K. Christopoulos[1,3]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504
[2]Department of Chemistry, University of Athens, Athens, Greece 15771
[3]Institute of Chemical Engineering and High Temperature Processes, Foundation of Research and Technology Hellas, GR-26504 Patras, Greece

E-mail: kalogian@upatras.gr

P1-41

Food allergies are defined as an immune response to food proteins. Food allergens present in foodstuffs have to be labelled according to the European Union. Food industry has established internal threshold values referring to allergens added by recipe, as well as allergens present due to cross-contamination. Many analytical methods have been reported for the detection of various allergens based on its protein or nucleic acid content. However, intensive processed and heat-treated foods are characterized by a higher degradation of proteins compared to DNA. Thus, DNA is preferred due to the fact that is efficiently extracted from food matrices and is less affected by extraction conditions or food procession as compared to proteins. In recent years, the number of proposed DNA methods for food allergen detection has been raised. The aim of this study is the detection of various nuts that are present even in traces in foods. The method involves the amplification of specific DNA sequences of nuts' genome by Polymerase Chain Reaction (PCR) and a subsequent chemiluminescent hybridization assay on microtiter wells. The detection and confirmation of the particular sequences of double stranded DNA is based on labeled oligonucleotide-probes, specific for each nut. In details, each amplified PCR product, that is biotinylated, is hybridized to the specific oligonucleotide-probe, which carries a poly(dA) tail at one end. The hybrids are then captured by poly(dT) sequences immobilized on the microtiter wells and detected by a streptavidin-alkaline phosphatase conjugate (SA_ALP) via streptavidin-biotin interaction. Finally, the chemiluminometric substrate of ALP, PPD (4- methoxy-4-(3-phosphatephenyl) spiro[1,2-dioxetane-3,2'-adamantane], disodium salt), is added and the produced chemiluminescence is measured by a luminometer. The intensity of the measured chemiluminescence is proportional to the concentration of the corresponding DNA sequence. The method was applied for the detection of peanut, hazelnut and walnut. The limit of detection of the proposed method was 1.4 pM for all the three DNA sequences. The method was also applied successfully for the detection of the three allergens in unprocessed and processed food such as cookies. Different mixtures of cookies were prepared that contained all the three different nuts in proportions varied from 0.01% to 5%. As low as 0.01% of each nut present in the cookie mixtures were detected by this method. The method can also be used for polyanalytical tests for the simultaneous detection of different DNA sequences.

Quantitative Structure-Chemiluminescence Intensity Relationships of 4-substituted phenols acting as luminol signal enhancers

N. Kritikos, Y. L. Loukas and Y. Dotsikas

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Athens, Panepistimioupoli Zografou GR - 157 71, Athens, Greece

E-mail: idotsik@pharm.uoa.gr

P1-42

Chemiluminescence-based analytical methods have been gaining ground in contemporary bioanalysis. The signal of classical systems like the luminol-horseradish peroxidase-hydrogen peroxide combination is significantly increased by the addition of an enhancer. Depending on the compound selected, sensitivity of the enhanced chemiluminescence methods due to signal amplification may increase by a 10- to 100- fold, while an increase in duration and stability is also observed. Among the various classes of compounds thus employed, 4-substitued phenols are a popular decent choice [1]. The group includes numerous members, differing in the substituent inserted on the phenolic core, from single halogen atoms, to small groups and aliphatic chains, to larger aromatic systems. Previous studies have explored the contribution of the substituent on their enhancing potency, yet no quantitative structure – property relationships (QSPR) employing molecular descriptors has been presented [2].

The current study explored the relationship between molecular structure and experimentally observed signal intensity of 24 such compounds through linear regression based methods of multivariate statistical analysis. More specifically, Projection to Latent Structures – Discriminant Analysis (PLS-DA) was first employed for their classification into a total of four classes, exhibiting different behavior. To be then followed by the construction of a QSPR PLS model based on the two, distinct yet closer in chemical space, classes. The resulting model was validated, through internal cross-validation leave-more-out procedures, the $Q^2_{ext(F3)}$ test-set based metric and Roy's, model stability and validity assessing, $r^2_{m(Av)}$ & $r^2_{m(\delta)}$, to evaluate quality and stability in predictions of signal intensity. Furthermore, recognizing the structural characteristics linked to the molecular property, the current study may provide insight to the recognition of novel enhancers of the same chemical group.

References

[1] Y. Dotsikas and Y.L. Loukas, *Talanta* 71 (2007) 906-910.
[2] A.R. Katritzky, V.S. Lobanov and M. Karelson, *Chem. Soc. Rev*., 24 (1995) 279-287.

Antimicrobial peptides and lipid-membranes interactions investigations in the Far-Infrared region

A. Hornemann[1], D. Eichert[2], A. Hoehl[1], M. Andersch[1], P. Emmer[1], B. Tiersch[3], M. Ryadnov[4], G. Ulm[1] and B. Beckhoff[1]

[1] Physikalisch-Technische Bundesanstalt, Abbestrasse 2-12, 10587 Berlin, Germany
[2] Elettra – Sincrotrone Trieste, S.S. 14 Area Science Park, 34149 Basovizza, Trieste, Italy
[3] Universitaet Postdam, Karl Liebknecht Strasse 24-35, 14476 Postdam, Germany
[4] National Physics Laboratory, Hampton Road, Teddington, Middlesex TW11 0LW, United Kingdom

E-mail: diane.eichert@elettra.eu

P1-43

Synchrotron radiation based infrared spectroscopy (SR-FTIR) offers the opportunity to explore vibrational information delivered by bio-molecular species in complementary spectral ranges, namely from mid to far or even THz ranges, where specific vibrational mechanisms await to be unraveled and new molecular science to be addressed.

Peptide therapeutics has received recently a renewed interest for their potentiality to challenge traditional small molecules drugs and for their broad range of applications from virology to oncology, or microbiota. Antimicrobial peptides (AMPs) in particular are developed as novel agents for compensating antibiotic increasing resistance by destabilizing microbial membranes. Also called host defense peptides, their clinical and commercial development still present some critical limitations, such as potential toxicity, susceptibility to proteases or to undergo molecular structure transitions and high production costs. In order to overcome these obstacles, new characterization methods, such as far-FTIR, are needed to study structural and functional integrity in their formulation. Specifically, AMPs' molecular specificities, related structure, control and function are still to be fully understood, both separately and globally.

In that framework, defined antimicrobial peptide templates and their interactions with lipid membranes models have been investigated in the 400 - 40 cm^{-1} spectral range, nearby the THz region. Fundamental information on far-FTIR spectroscopic signatures of peptides native molecular organization, on membranes and on peptides-lipid layers coupling is provided. In particular, T-dependent spectroscopic analysis, supported by 2D correlative tools evidenced positive interactions between selected customized AMPs and artificial membranes systems, thus demonstrating molecular structure - bioactivity relationships.

Far-FTIR spectroscopy ascertains its high potential for the development and characterization of new antimicrobial agents optimized at the peptide sequential level, as well as for the investigation of their triggered biological effects. In such, Far-FTIR can contribute significantly in the understanding of antimicrobials peptides modes of action and in the follow up of their performance.

References

[1] A. Hornemann, D. Eichert, A. Hoehl, M. Andersch, P. Emmer, B. Tiersch, M. Ryadnov, G. Ulm and B. Beckhoff, *Biochimica et Biophysica Acta – Biomembranes* (2015) submitted.

The X-ray Fluorescence beamline at Elettra – Sincrotrone Trieste: new characterization opportunities for nano-structured materials

D. Eichert[1], L. Luehl[1,2], F. Brigidi[1], A. Gambitta[1] and W. Jark[1]

[1] Elettra – Sincrotrone Trieste, S.S. 14 Area Science Park, 34149 Basovizza, Trieste, Italy
[2] Technische Universitaet Berlin, IOAP, Hardenbergstrasse 36, 10623 Berlin, Germany

E-mail: diane.eichert@elettra.eu

P1-44

The XRF beamline at Elettra–Sincrotrone Trieste [1] is conceived as a multi-purpose beamline designed to accommodate a variety of end-stations dedicated to e.g. X-ray Spectrometry, Total Reflection XRF (TXRF) or microscopy techniques. Located at a bending magnet source, its monochromator is presently covering the photon energy range 3.6 - 14 keV, with a resolving power of 1.4 10^{-4} (Si(111)). The source is re-imaged to a 250 X 50 □m beamsize (hor X vert) in an exit slit, with an angular divergence of 0.15 mrad and a transmitted flux of about 5 10^{9} ph/s (5.5 keV, 2GeV). In the near future the excitation energy range of the beamline will be extended down to 2 keV, and multilayer coatings will increase the photon flux on the expense of a similarly increasing band width, however crucial for many applications.
The XRF beamline is presently hosting and operating in collaboration with the IAEA an Ultra-High-Vacuum Chamber (UHVC), based on a prototype [2] designed and built by Physikalisch-Technische Bundesanstalt (PTB) and Technische Universitaet Berlin (TUB). This UHVC includes a motorized 5-axis sample manipulator allowing 3 linear translations (x/y/z) and 2 rotational (theta/phi) degrees of freedom for the sample. An independent 2theta goniometer coupled with another linear axis allows performing X-ray reflectometry measurements. The aim is to use tunable synchrotron X-rays with ~200 □m beam size for various X-Ray Spectrometry techniques such as: TXRF, Grazing Incidence/Exit XRF (GI-XRF/GE-XRF), X-Ray Reflectometry (XRR) or X-ray Absorption Spectroscopy (XAS).
A description of the beamline, analytical developments, and commissioning results will be presented to demonstrate the performance parameters for TXRF, GIXRF, XRR and combined XRF methods – XAS (X-ray Absorption Spectroscopy such as XANES and EXAFS) as well as the beam quality needed for advanced analysis.
Highlights will be put on experimental data obtained during pilot research experiments in the field of novel nanostructured layered materials and illustrate the manifold possibilities that the setup offers to analyze nanoscale samples.

References

[1] W. Jark, D. Eichert, L. Luehl and A. Gambitta *Proceedings of SPIE, Vol. 9207 Advances in X-Ray/EUV Optics and Components IX* (2014**)** 92070G - 12. *doi: 10.1117/12.2063009*.
[2] J. Lubeck, B. Beckhoff, R. Fliegauf, I. Holfelder, P. Hoenicke, M. Mueller, B. Pollakowski and F. Reinhardt, *J. Weser Review of Scientific Instruments, 84* (2013) 045106-1 -7.

Fluorescent detection of biothiols and SO_2 derivates via Michael addition reaction of it to isoxasole

M. Gómez, M. E. Aliaga, C. Irribarren, A. Cañete and E.G. Perez

Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile

E-mail: mtgomez@uc.cl

P1-45

Variations in the levels of biologically important thiols, such as cysteine (Cys), homocysteine (Hcy), cysteinyl-glycine (Cys-Gly), γ-glutamyl-cysteine (γ-Glu-Cys) and glutathione (GSH), can cause or are indicative of some health problems [1]. On the other hand, sulfur dioxide (SO_2) is commonly used as an antioxidant and antimicrobial in many processed foods. Despite its widespread use and proven as a preservative, SO_2 derivatives (sulfite and bisulfite species) are attributed various adverse health effects associated with their intake [2]. Therefore, nowadays their determination and quantification is an area of rapid development [3].
In this work, we have synthesized dimethyl-{4-[2-(3-methyl-4-nitro-isoxazol-5-yl)-vinyl]-phenyl}-amine (**1**), which structure is shown in Fig. 1. The aim is to use this compound as fluorescent probe for biothiols and/or SO_2 derivatives, taking advantage of the electrophilic character of **1** in reactions such as Michael additions.

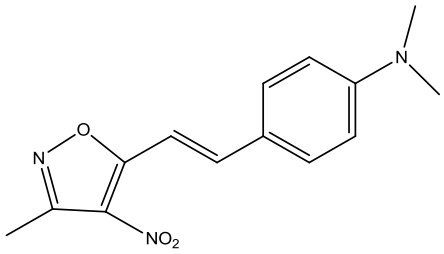


Fig. 1: The structure of the tested probe **1**.

Thus, in this work we characterize this compound (^{1}H- NMR, ^{13}C-NMR and ESI-MS), and we undertake a kinetic investigation of its behavior as sensor for biothiols and/or SO_2 derivatives. We found that this probe displays a high selectivity for sulfite over the other tested biothiols.

Acknowledgements: This work was supported by FONDECYT Postdoc Grant #3150196, FONDECYT Grant #1130062 and FONDEQUIP EQM120163.

References

[1] A. Meister and M.E. Anderson, *Annu Rev Biochem.*, 50 (1983) 711-760.
[2] C. Wang, S. Feng, L. Wu, S. Yan, C. Zhong, P. Guo, R. Huang, X. Weng and X. Zhou, *Sensors Actuat B-Chem*, 190 (2014) 792–799.
[3] Y. Yang, F. Huo, C. Yin, A. Zheng, J. Chao, Y. Li, Z. Nie, R. Martínez-Máñez and D. Liu, *Biosens Bioelectron*, 47 (2013) 300-306.

Formation of Au@Ag core-shell nanorods as an approach to spectrophotometric determination of catecholamines

M. Gorbunova, L. Zamurueva, V. Apyari and S. Dmitrienko

Division of Analytical Chemistry, Chemistry Department of M.V. Lomonosov Moscow State University, Leninskie gory, 1/3, 119991 Moscow, Russia

E-mail: masha13_1992@mail.ru

P1-46

Gold nanoparticles are widely used in various fields of analytical chemistry due to their unique optical properties conditioned by the surface plasmon resonance (SPR), which causes intense absorption in the visible spectral region. Spherical gold nanoparticles are usually used in analysis. There are much less investigations devoted to non-spherical nanoparticles. Meanwhile, the extra optical properties of non-spherical gold nanoparticles, for example, nanorods (AuNRs), caused by the presence of several modes of the surface plasmon oscillations, and several bands of the surface plasmon resonance could play a significant role in the development of new methods for determination of different compounds.

The aim of this study was to investigate the possibility of using AuNRs for spectrophotometric determination of catecholamines based on formation of Au@Ag core-shell NRs.

Synthesis of AuNRs was carried out in the presence of hexadecytrimethylammonium bromide. The AuNRs were characterized by transmission electron microscopy and spectrophotometry. There are two maxima in absorption spectra of AuNRs: at 520 and 700 – 750 nm, which correspond to the transverse and longitudinal plasmon oscillations, respectively.

The interaction of catecholamines with silver nitrate in the presence of AuNRs results in reduction of silver ions and formation of a silver layer on the surface of AuNRs. This process lead to a hypsochromic shift of the long-wavelength maximum in the absorption spectrum, and to a change of the color from pale-pink to green. The interaction of AuNRs with adrenaline, noradrenaline, dopamine and dobutamine was studied. The reaction occurred completely in less than a minute, the most complete interaction was observed at pH 9.0 – 9.5.

The dependences of the long-wavelength SPR band maximum shift ($\Delta\lambda$, nm) on the concentration of catecholamines were represented as curves with a bend, which presumably caused by changes in morphology of the surface silver layer and spontaneous nucleation of silver nanoparticles. These dependences can be used as non-linear calibration curves for the determination of catecholamines. The limits of detection are decreased as follows: dobutamine > adrenaline > noradrenaline > > dopamine, and are equal to 0.07, 0.04, 0.04, 0.03 μg mL^{-1}. The relative standard deviation does not exceed 7 %. Effects of amino acids, organic and inorganic ions on the determination of catecholamines were studied. Accuracy of the determination was confirmed by the analysis of a pharmaceutical formulation.

Acknowledgements: This work was financially supported by the Russian Foundation for Basic Research (grant N 14-03-31109 mol_a)

Preliminary results of the chemical composition of deep sea sediments from the greater area of Santorini

S. Foteinis[1], N. Kallithrakas-Kontos[1] and C. Anagnostou[2]

[1]Technical University of Crete, Analytical and Environmental Chemistry Laboratory, University Campus, GR-73100 Chania, Greece
[2]Hellenic Centre for Marine Research, Institute of Oceanography, 46.7km Athens-Sounio Avenue, 19013 Anavyssos, Greece

E-mail: kalli@mred.tuc.gr

P1-47

The greater area of Santorini has been in the main focus of the scientific community during the last decades due to its unique characteristics, namely volcanism and hydrothermal activity in convergent settings of the thinned continental crust of the Hellenic subduction system (Druitt et al., 1999 [1], Kilias et al, [2]). Volcanic activity is closely related to submarine hydrothermal activity, which results to the deposition of a vast number of elements, among them various metals including heavy metals, rare earths etc. Deposition depends on various factors, including hydrothermal fluid composition, chemical reactions between precipitates and water, conditions during seawater-basalt interaction (e.g. temperature and permeability) and subsurface mixing (Douglas et al, 1985 [3]). Since, the geochemical composition of deep sea sediments of the greater of Santorini is still largely unexplored, in this work we present preliminary results of the chemical composition of deep sea sediments, using box and gravity sediment cores collected by the Hellenic Centre for Marine Research HCMR. The length of each core ranges from 10 up to 70 cm, whilst the water depth acquired from ranges from 88 to 1862 m. An Energy Dispersive X-Ray Fluorexcence (EDXRF) unit was used for sample analysis and evaluation, using an Am-241 (photon energy of 59.6 keV and 458 year half-life) as excitation source and a Si-PIN X-Ray Detector. The cores were assessed in terms of the vertical and spatial distribution of Ca, Mn, Fe, Sr, Zr, as well as of Ce and La, and our preliminary results indicate that the majority of the cores are enriched with these elements.

References

[1] T.H. Druitt, L. Edwards, R.M. Mellors, D.M. Pyle, R.S.J. Sparks, M. Lanphere, M. Davies and B. Barreiro, Santorini volcano, Memoir 19, Geological Society, London, 1999. ISBN 1 86239 048 7

[2] S. P. Kilias, P. Nomikou, D. Papanikolaou, P.N. Polymenakou, A. Godelitsas, A. Argyraki, S. Carey, P. Gamaletsos, T.J. Mertzimekis, E. Stathopoulou, J. Goettlicher, R. Steininger, K. Betzelou, I. Livanos, C. Christakis, K. Croff Bell and M. Scoullos, New insights into hydrothermal vent processes in the unique shallow-submarine arc-volcano, Kolumbo (Santorini), Greece, Scientific Reports (2013) 3, Article number: 2421

[3] D. E. Ruhlin and R.M. Owen, *Geochimica et Cosmochimica Acta* 50 (1985 393-400.

Sulphur Speciation by a Si-PIN X-ray detector

N. Kallithrakas-Kontos and R. Moschochoritou

Technical University of Crete, Analytical and Environmental Chemistry Laboratory, University Campus, GR-73100 Chania, Greece

E-mail: kalli@mred.tuc.gr

P1-48

X-ray energy shifts (centroid shifts) have been measured in the past by using energy dispersive X-Ray spectrometry (EDXRS) for chromium, manganese [1] and vanadium [2] analysed elements and compounds; the possibility of the discrimination of different chemical states by EDXRS has also cross evaluated in the past with a carefully controlled electric signal processing [3]. The energy shifts are originated from speciation differences in oxidation number (electronic environment) of the examined element. Sulphur is an element with a wide variation in its oxidation numbers as well as with an M electron valence shell, so it can be quite sensitive in x-ray shift effects. Various sulphur compounds were examined (including elemental sulphur, sodium sulphate and hydrated $Na_2SO_4.10\ H_2O$) and the effect of the sulphur speciation on its Ka x-ray centroid was estimated. An AMPTEK Mini-X X-Ray Tube System (at 25 kV/10 μA, with a silver-Ag target) was used for compound excitation combined with an AMPTEK X-123 complete X-Ray spectrometer with Si-PIN detector (133 eV Full width half maximum at sulphur Ka x-ray energy). 3.83 eV/channel and prolonged collection time (of the order of 1 hour) were used in order to achieve adequate statistic. The results show the possibility to determine small effects (lower than 1 eV) in the sulphur compounds as a function of its speciation.

References

[1] N. Kallithrakas-Kontos, *Spectrochimica Acta B*, 51 (1996) 1655-1659.
[2] N. Kallithrakas-Kontos and R. Moschochoritou, *X-Ray Spectrometry*, 27 (1998) 173-176.
[3] Y. Xiao, S. Hayakawa, Y. Gohshi, M. Oshima, *Analytical Sciences*, 14 (1998) 1139-1144.

New possibilities for prediction of cereals' and pseudo-cereals' chemical and technological parameters by near-infrared spectroscopy

É. Kónya[1], T. Halasi[2], P. Forgó[3], Zs. Cserhalmi[1], N. Adányi[1] and A. Kiss[1]

[1] Food Science Research Institute, National Agricultural Research and Innovation Centre, H-1022 Budapest, Herman Ottó Str. 15
[2] GoodMills Magyarország Malomipari Zrt., H-2900 Komárom, Klapka György Str.. 40
[3] Eger Innovations Nonprofit Kft., H-3300 Eger, Leányka Str.. 6

E-mail: e.konya@cfri.hu

P1-49

Near-infrared spectroscopy has many advantages what make it a widely used analytical method in the different areas, like agricultural and food industry as well. Analyses and methods in quality determination require more sample, time, work and cost, thus quality control needs rapid, reliable tools. For good accuracy in prediction of chemical and technological parameters a complex work with reference measurements and spectral measurements should be carry out. Nowadays in cereals' and pseudo-cereals' quality chemical parameters determination has importance still at harvest on the field. In wheat quality not only chemical parameters, but technological characteristics has more importance. Prediction of cereals compositional parameters by near-infrared spectroscopy has good accuracy, the correlation coefficient of such calibration models are higher than 0.8, but for pseudo-cereals only a few study known. In case of technological, mostly rheological parameters the accuracy of prediction is still lower.

In this research our aim was to analyse different cereals (wheat, oat, rye) and pseudo-cereals (amaranth, buckwheat) by near-infrared spectroscopy, collecting their own spectra. The compositional characteristics (moisture, protein, fat content) measurements of flours were carried out by standard analytical methods, and rheological parameters were determined by alveograph and valorigraph in case of wheat.

Principal component analysis was carried out to find out possible separation in the sample group. Only the different species showed individual groups, but in case of each species we could use the whole set of samples.

Partial least squares regression with different math treatments (first and second derivatives, SNV, SNV+Detrend) was applied for developing calibration equations. In case of compositional data, the calibration models' correlation coefficient was between 0.8-0.9, and for rheological parameters it was between 0.6-0.7. The chemical parameters could be predicted by near infrared spectroscopy with good accuracy, but the rheological properties only with enough accuracy.

Acknowledgements: Project number: AGR_PIAC_13-1-2013-0048

A new type of X-ray spectrometry UHV instruments at the SR facilities BESSY II, ELETTRA and SOLEIL

J. Lubeck[1], B. Boyer[2], B. Detlefs[3], D. Eichert[4], R. Fliegauf[1], D. Grötzsch[5], I. Holfelder[1], P. Hönicke[1], W. Jark[4], R. Kaiser[6], B. Kanngießer[5], A.G. Karydas[6], J.J. Leani[6], M.C. Lépy[2], L. Lühl[4,5], Y. Ménesguen[2], A. Migliori[6], M. Müller[1], B. Pollakowski[1], M. Spanier[5], G. Ulm[1], J. Weser[1] and B. Beckhoff[1]

[1] Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin, Germany
[2] CEA, LIST, Laboratoire National Henri Becquerel, Bât. 602 PC 111, CEA-Saclay 91191 Gif-sur-Yvette cedex, France
[3] CEA-LETI, Minatec Campus, 17 rue des Martyrs, 38054 Grenoble, France
[4] Elettra - Sincrotrone Trieste (EST) S.C.p.A., 34149 Basovizza, Trieste, Italy
[5] Technische Universität Berlin, Institut für Optik und Atomare Physik, Hardenbergstr. 36, 10623 Berlin, Germany
[6] Nuclear Spectrometry and Applications Laboratory, IAEA Laboratories, A-2444, Seibersdorf, Austria

Email: janin.lubeck@ptb.de

P1-50

A novel type of ultra-high vacuum instrument for X-ray reflectometry and spectrometry related techniques for nanoanalytics by means of synchrotron radiation has been constructed and commissioned at BESSY II [1]. This versatile instrument was developed by the Physikalisch-Technische Bundesanstalt, Germany's national metrology institute, and includes a 9-axis manipulator that allows for an independent alignment of the samples with respect to all degrees of freedom. In addition, a rotational and translational movement of several photodiodes as well as a translational movement of a beam geometry defining aperture system is provided. Thus, the new instrument enables various analytical techniques based on energy dispersive X-ray detectors such as reference-free X-Ray Fluorescence (XRF) analysis, total-reflection XRF, grazing-incidence XRF, in addition to optional X-Ray Reflectometry (XRR) measurements or polarization-dependent X-ray absorption fine structure analyses. Samples having a size of up to 100 mm x 100 mm can be analyzed with respect to their mass deposition, elemental, spatial or species composition with respect to surface contamination, nanolayer composition and thickness, the depth profile of matrix elements or implants, nanoparticles or buried interfaces as well as the molecular orientation of bonds.
Three technology transfer projects of adapted instruments have enhanced X-Ray Spectrometry (XRS) research activities within Europe at the synchrotron radiation facilities ELETTRA (IAEA) and SOLEIL (CEA/LNE-LNHB) as well as at the X-ray innovation laboratory BLiX (TU Berlin) where different laboratory sources are used. Here, smaller chamber requirements led PTB in cooperation with TU Berlin to develop a modified instrument equipped with a 7-axis manipulator: reduced freedom in the choice of experimental geometry (absence of out-of-SR-plane and reference-free XRS options) has been compensated by encoder-enhanced angular accuracy for GIXRF and XRR. Selected applications of these advanced ultra-high vacuum instruments demonstrate its flexibility, capabilities and reliability.

References

[1] J. Lubeck, B. Beckhoff, R. Fliegauf, I. Holfelder, P. Hönicke, M. Müller, B. Pollakowski, F. Reinhardt, and J. Weser, *Rev. Sci. Instrum.*, 84, 2013, 045106.

Optical waveguide lightmode spectroscopy technique-based immunosensor development for aflatoxin B_1 determination in spiced paprika samples

K. Majer-Baranyi[1], Zs. Zalán[1], M. Mörtl[2], A. Székács[2], I. Szendrő[3] and N. Adányi[1]

[1]Food Science Research Institute, National Agricultural Research and Innovation Centre, Budapest, Herman Ottó str. 15. H-1022
[2]Agro-Environmental Research Institute, National Agricultural Research and Innovation Centre, Budapest, Herman Ottó str. 15. H-1022
[3] MicroVacuum Ltd. Budapest Kerékgyártó u. 10. H-1147

E-mail: k.baranyi@cfri.hu

P1-51

Aflatoxins are naturally occurring mycotoxins that are produced by the fungus *Aspergillus*, which can contaminate food crops such as peanuts, grains, dried nuts and spices. Aflatoxins are highly toxic and carcinogenic to human health, therefore efforts have been made toward the development of rapid and sensitive methods for the detection of this compound. In our investigation, optical waveguide lightmode spectroscopy (OWLS) technique has been applied to label-free detection of aflatoxin B_1 in competitive immunoassay format using aflatoxin B_1-specific polyclonal antibodies. After immobilizing the antigen conjugate for the indirect measurement, the sensor chip was used in a flow-injection analyzer (FIA) system. For competitive sensor investigation with the sensitized chip, first the optimal dilution rate of polyclonal antibodies was determined. For the measurements, antibody stock solution was diluted to a 1:400 dilution. The competitive OWLS sensor was also optimised for the sensitising antigen concentration where aflatoxin-BSA conjugates were investigated in different concentrations. According to our result the best signal responses were obtained when 5 µg/ml aflatoxin conjugate was immobilized on the surface. During the competitive measurement, standard solutions were mixed with the antibodies at the appropriate concentration, and the mixture was incubated for 1 min and injected into the OWLS system. With the established indirect method paprika samples from different countries were investigated. Aflatoxin B_1 content of paprika samples originated from Hungary, China, Serbia, Spain, Peru, Brazil and Bulgaria were investigated. The results obtained with the OWLS method were compared with those of the HPLC and ELISA measurements. The regression coefficient was calculated as 0.96 comparing the results from the indirect immunosensor to that obtained by HPLC. According to our results the competitive OWLS immunosensor has a potential for quick determination of aflatoxin B_1 in paprika samples.

Acknowledgements: This research was executed in the framework of the EU-project SPICED (Grant Agreement: 312631) with the financial support from the 7th Framework Programme of the European Union; as well as project NUKR.SFPP 984637 in the NATO SPS Programme. This publication reflects the views only of the authors, and the European Commission cannot be held responsible for any use which may be made of the information contained therein.

The quantitative analysis of ternary mixtures of anhydrous crystalline $CaCO_3$ polymorphs using micro Raman spectroscopy

R. Ševčík, P. Mácová and M. Pérez-Estébanez

[1]Institute of Theoretical and Applied Mechanics ASCR, Centre of Excellence Telč, Batelovská 485-486, 588 56 Telč, Czech Republic

E-mail: sevcik@itam.cas.cz

P1-52

Many studies are focused on the calcium carbonate ($CaCO_3$) due to its significance in nature systems and the widespread use in the industry. $CaCO_3$ occurs in the three anhydrous crystalline polymorphs (calcite, aragonite and vaterite) and two hydrated crystal forms ($CaCO_3.6H_2O$ (ikaite) and $CaCO_3.H_2O$). Amorphous $CaCO_3$ is also known [1]. In this work, the quantification of ternary mixture (aragonite, calcite and vaterite) was accomplished using micro Raman spectroscopy. $CaCO_3$ polymorphs were synthetized through the reaction between aqueous solutions of $CaCl_2.2H_2O$ and K_2CO_3 with modified procedure as published elsewhere [2]. Raman spectra were collected employing the DXR Raman spectrometer (Thermo Scientific) equipped with high resolution grating (1800 lines mm^{-1}). The laser beam (= 532 nm) was focused with 20x objective and the map of the area 180x180 μm (100 points) was measured from each well homogenized sample in the spectral range 1800-50 cm^{-1}. 20 exposures of each spectrum were recorded with exposure time 2 s and 10 mW power on the sample. The Raman bands at 700.8, 711.4, 750.0 cm^{-1} were used for quantitative analysis of aragonite, calcite and vaterite, respectively. The determined intensities at these specific Raman bands were statistical treated and the calibration plots were made as described in [3]. All measured samples were simultaneously measured using X-ray powder diffraction and quantitative phase analysis was performed with the Rietveld method to confirm the concentrations of prepared mixtures. The validity of the method was tested on the sample mixture of 18.3(2) wt.% aragonite, 42.8(5) wt.% calcite, 39(2) wt.% vaterite and the relative errors were determined to be less than 4 % for all species.

Acknowledgments: The authors gratefully acknowledge support from the Czech Grant Agency GA ČR grant 14-20374P and the project No. LO1219 under the Ministry of Education, Youth and Sports National sustainability program I of Czech Republic.

References

[1] F.C. Meldrum and H. Cölfen, *Chem. Rev.*, 108 (2008) 4332-4432.
[2] A. Sarkar and S. Mahapatra, *Cryst. Growth Des.*, 10 (2010) 2129-2135.
[3] C. G. Kontoyannis and N.V. Vagenas, *Analyst*, 125 (2000) 251-255.

Sequential injection method for determination of gamma-aminobutyric acid based on nanoparticle second order light scatterring

S. Teerasong[1,2], A. Jinnarak[2] and D. Nacapricha[1,3]

[1]Flow Innovation-Research for Science and Technology Laboratories (FIRST Labs.), Thailand
[2]Department of Chemistry and Applied Analytical Chemistry Research Unit, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
[3]Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

E-mail: ktsaowap@kmitl.ac.th

An automated sequential injection (SI) was developed for on-line determination of gamma-aminobutyric acid (GABA). The reaction is based on the aggregation of citrate capped silver nanoparticles (AgNPs) triggered by GABA, causing a change in the particle size which influences the degree of second order light scattering [1]. At pH 3.6, GABA is positively charged. When dispersed into the AgNPs solution, it induces the particles to aggregate via electrostatic interaction. This results in the second order light scattering variation which can be monitored by using a spectrofluorometer. Solutions of GABA, acetate buffer and AgNPs were sequentially introduced into a holding coil of the SI system. The solution zone was then transferred to the spectrofluorometer, set with excitation and detection wavelengths at 300 and 600 nm, respectively. Under optimum condition a linear calibration in range of 50-200 mg L^{-1} GABA was achieved with detection limit of 30 mg L^{-1}. Good precision of analysis was attained (RSD = 0.6%). The developed method was successfully applied for the determination of GABA in food samples with throughput of 25 samples h^{-1}.

References

[1] C.C. Wang, M.O. Luconi, A.N. Masi and L.P. Fernandez, *Talanta*, 77 (2009) 1238-1243.

Multicommutation flow system for manganese speciation in water samples by solid phase extraction – flame atomic absorption spectrometry

A. Tobiasz, M. Sołtys, D. Dudek-Adamska, and S. Walas

Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena St. 3, 30-060 Krakow, Poland

E-mail: tobiasz@chemia.uj.edu.pl

P1-54

For speciation analysis often hyphenated techniques are applied, mainly chromatographic methods combined with inductively coupled plasma mass spectrometry (ICP MS). In contrast, also much simpler, and low cost techniques like flame atomic spectrometry can be used whenever analytes separation will be connected with its preconcentration eg. by solid phase extraction (SPE).
Conventional SPE technique allows determination of only one analyte form in one experiment. Adaptation of typical SPE setup for speciation analysis requires in the simplest use a two-step procedure: direct determination of one form and total analyte determination after sample conversion.
Alternatively, a sorbent indicating two/few types of functional groups, a mixture of different sorbents filled in one column or columns in tandem can be applied. In this case each species may be eluted with different (selected) eluents.
Herein for separation of manganese(II)/(VII) forms two different sorbents were proposed: activated silica gel for Mn^{2+} and anion exchange resins for manganese anion. The speciation analysis was conducted in flow multicommutation system comprising three directional valves, column filled with sorbent and peristaltic pumps. Flow programme consist of following steps: filling tubes with sample, loading of analytes on sorbent, washing of sample residues from system and finally elution of each form. For both analytes detailed evaluations of preconcentration conditions were performed: a type and concentration of an eluent, pH of a sample, a loading time and method resistance to interference effects.
The proposed method was successfully applied to speciation analysis of manganese in water samples.

Acknowledgements: The research concerning the reference method was carried out with the equipment purchased, thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.0100-12-023/08).

Fingerprinting analysis of Romanian berries using TLC and UV-VIS spectrometry

I.-A. Sima

Babes-Bolyai University, Faculty of Chemistry and Chemical Engineering, Department of Analytical Chemistry, Arany Janos 11, 400028, Cluj, Romania

E-mail: ioanatuhutiu@ymail.com

P1-55

Thin-layer chromatography (TLC) and UV-Vis spectrometry, coupled with advanced chemometric techniques have been investigated in order to fingerprint some local Romanian berries extracts. The study was conducted using extracts of sea-buckthorn (Hippophae rhamnoides), bilberry (Vaccinium myrtillus), cranberry (Vaccinium oxycoccos), rose hip (Cynosbati fructus), blackthorn (Prunus spinosa), raspberry (Rubus idaeus), Cornelian cherry (Cornus mas) and blackberry (Rubus fruticosus), all acquired from local markets. The extraction solvent was optimized to increase the extraction of flavonoids and polyphenols and the best results were obtained using a mixture of ethanol-water 70:30 (v/v). Then the extracts were firstly subjected to chromatographic separation coupled with digital image analysis and secondly to spectrophotometric analysis. In both cases the obtained results (digital chromatograms and spectra) were digitized and evaluated using multivariate exploratory techniques.

Adulteration of extra virgin olive oils with seed oils studied with Optical Spectroscopy

A. Papadaki, A. Philippidis and M. Velegrakis

Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1385, GR-711 10 Heraklion, Crete, Greece

E-mail: vele@iesl.forth.gr

P1-56

Extra virgin olive oil (e.v.o.o.) is considered to be the most valuable oil for the human nutrition, due to the lower levels of unsaturated fatty acids and the higher presence of vitamin E when compared to the seed oils. The latter superior properties of e.v.o.o not only increase its cost, but also render it vulnerable to adulteration processes using common seed oils [1]. In order to identify the purity level of e.v.o.o., we have generated mixtures using Cretan e.v.o.o. and seed oils, which were subsequently measured by employing the well-established methodologies of UV/Vis Absorption and Fluorescence Spectroscopy.

More specifically, by measuring the absorbance of oil mixtures in the UV region of the spectrum, we have determined the indices K_{270} and ΔK (which comprise reliable quality indicators [2]) and discriminated the highly pure e.v.o.o. among the adulterated ones. In addition, our results in the visible region (400-800nm) indicate that the discrimination of the oils can be achieved through the absorbance peak detection at 414 nm, where the caretonoids group presents intense absorption.

Moreover, by employing the Fluorescence Spectroscopy technique, representative excitation-emission maps have been generated for each case. It has been observed, that the relative variance of chlorophyll's fluorescence intensity levels is mainly responsible for the differentiation of the adulterated oils from the pure ones. Furthermore, the determination of the lower limits for e.v.o.o. adulteration of these methods are investigated and discussed.

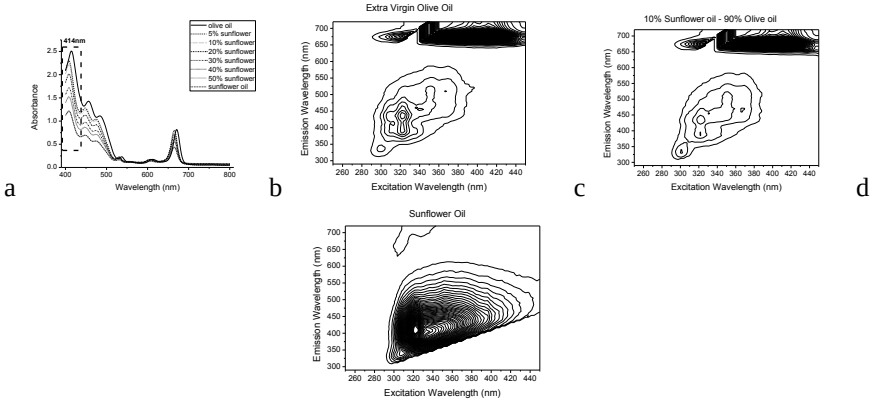


Fig. 1: Adulteration of oils a. Absorption spectra in visible region, b-d. Maps of pure oils and a mixture of them

References

[1] D. Boskou, *AOCS Press*, Chapter 8 (1996) 121-133

[2] Dubravka Skevin et.al. , Croatian Journal of Food Technology, Biotechnology and Nutrition, 6 (3-4), (2011) 117-122

Ligand-free cation-selective biomimetic sensors prepared from phospholipid-polydiacetylene mixed vesicles

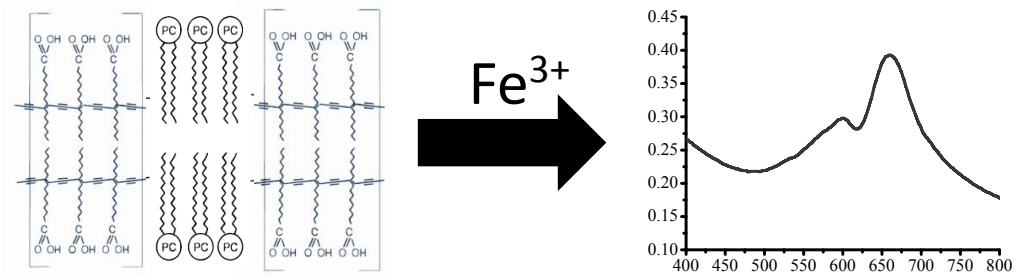
V.A. Gatselou, D.L. Giokas, G.Z. Tsogas and A.G. Vlessidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

E-mail: avlessid@cc.uoi.gr

P1-57

Molecular recognition of metal ions in artificial cell membranes typically involves the coordination of metals to ligands at the membrane surface (e.g. cell's acidic phospholipids complex calcium ions). In this work, we report a cation-selective sensor composed of phospholipid-polydiacetylene mixed vesicles which can selectively uptake Fe^{3+} ions without co-embedded ligands (receptors). Specifically, we observed that supramolecular assemblies of vesicles composed of phospholipids embedded in a matrix of polymerized diacetylene [PDA] lipids at an appropriate molar ratio undergo colorimetric changes in the presence of Fe^{3+} ions in solution. The blue-to-red color transitions of the vesicles are related to a complex binding of the Fe^{3+} cations to the phospholipid-PDA domain. It is demonstrated that this biomimetic system detects cations in submillimolar concentrations and affords good ionic selectivity, in particular between Fe^{3+} and other physiologically important and environmentally relevant ions.



Blue-Purple **Red**

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund.

Determination of dithiocarbamates with photochemically amplified chemiluminescence detection

V.A. Gatselou, D.L. Giokas, G.Z. Tsogas and A.G. Vlessidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

E-mail: avlessid@cc.uoi.gr

P1-58

Beyond their widespread use in the agricultural industry dithiocarbamates (DTCs), have also been used as vulcanization accelerators in the rubber industry, as antibacterial, antituberculosis and antifungal agents, as drugs for the treatment of alcohol abuse as well as for group transfer radical cyclization reactions in organic synthesis. Therefore, their determination over a wide concentration range and in different matrices is essential for environmental risk assessment, industrial process control as well as pharmaceutical quality assessment.

In this work, we present a new and simple method for the determination of dithiocarbamates (DTCs) including dimethyl-dithiocarbamates, ethylene-bisdithiocarbamates and propylenebisdithiocarbamates using chemiluminescence detection. The method relies on the enhancement of the luminol chemiluminescence signal, induced by radicals generated during the photodegradation of DTCs under UV light exposure. In this manner, a significant increase in the sensitivity is accomplished enabling the determination of DTCs at the low μg/L levels without sample preconcentration and with good precision (RSD< 2%).

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund.

Thiol-functionalized quantum dots as photoluminescent sensors for the determination and speciation of gold and silver nanoparticles after micelle mediated preconcentration

G. Z. Tsogas, D. L. Giokas and A.G. Vlessidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

E-mail: avlessid@cc.uoi.gr

P1-59

This work presents a new strategy for the determination and speciation of gold and silver nanoparticles at ultra-trace levels in environmental water samples. The developed method is based on their initial extraction and preconcentration in the micelles of a non-ionic surfactant medium and their subsequent separation through a selective uptake and dissolution process. CdS quantum dots possessing surface thiol ending groups were then used to bind the nanoparticles or their released precursor metal ions quenching the photoluminescent signal. A linear dose-response curve was established and the method was successfully applied to the fluorescence detection of gold and silver nanoparticles in environmental samples at the picomolar concentration levels.

Acknowledgments: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES. Investing in knowledge society through the European Social Fund.

A metabolic and antioxidant profile study of herbal infusions and decoctions

Ch. Fotakis[1], D. Tsigrimani[1,2], Th. Tsiaka[1,2], I. Strati[3], C. Makris[1,2], D. Tagkouli[1,2], Ch. Proestos[2], V.J. Sinanoglou[3], P. Zoumpoulakis[1]

[1]Institute of Biology, Medicinal Chemistry & Biotechnology, National Hellenic Research Foundation, 48, Vas. Constantinou Ave., 11635, Athens, Greece.
[2]Department of Chemistry, National and Kapodistrian University of Athens, Athens, 15771, Greece
[3]Department of Food Technology, Technological Educational Institution of Athens, Ag. Spyridonos Street, Aigaleo GR-12210, Athens, Greece

E-mail: pzoump@eie.gr

P1-60

This study implements NMR metabolomics and Spectrophotometry (DPPH, ABTS and Folin Ciocalteu assays) in order to put under the scope infusions and decoctions of herbal species stemming from Greece (9 samples) and of foreign origin (11 samples). The global and phenolic profiles assessed by NMR were evaluated and correlations were attempted with the spectrophotometric results. The primary objective was to determine in either preparations, categories of metabolites that contribute to their nutritional characteristics emphasizing in their antioxidant profile. Secondly, implementation of multivariate statistical analysis of experimental data, highlighted differences between herbal species, as well as between the infusions and decoctions in order to propose preparations which yield the highest nutritional benefits.

References

[1] Y. Wang, H. Tang, J.K. Nicholson, P.J. Hylands, J. Sampson, I. Whitcombe, C. G. Stewart, S. Caiger, I. Oru and E. Holmes, *Planta Medica*, 70 (2004) 250 -255.
[2] H.M. Heyman and J.J.M. Meyer, *South African Journal of Botany*, 82 (2012) 21–32
[3] H. K. Kim, Y. H. Choi and R.Verpoorte, *Nature protocols*, 5 (2010) 536 – 549.

Determination of the Adulteration of Extra Virgin Olive Oil by Means of FTIR Spectroscopy

E.G. Barbounis, K. Tampouris, D. Georgantas

N. ASTERIADIS S.A, Scientific Consulting Department.

e-mail: mb@asteriadis.gr

P1-61

The determination of food authenticity and the detection of adulteration are problems of increasing importance in the food industry. This is especially so for "value added products" where the potential financial awards for substitution with a cheaper ingredient are high. In this work the potential of Fourier Transform Infrared Spectroscopy combined with a Diamond Attenuated Total Reflectance attachment as a rapid analytical technique for the quantitative determination of adulterants in Extra Virgin Olive Oil (EVOO) is demonstrated.
The proposed method does not require sample preparation and eliminates the need for using organic solvents.
Experimental results showed that even if the spectral differences in the middle infrared spectral region are very small, because most vegetable oils contain the same type of fatty acids (especially those with C16 and C18) and triglyceride content is similar (C50, C52, C54), nevertheless, there are subtle spectral differences in the spectrum of various types of vegetable oils. This enables us to identify the addition of foreign oil in an oil sample using calibration curves established for certain characteristic frequencies in known mixed oils.

Tuesday 22 September 2015

Royal Cruise Hall-A

Chair: W. Frenzel, J. Kapolos

Mass Spectrometry/ Chromatography 1

Invited lecture

ICP MS in metallomics - state-of-the-art and perspectives

R. Lobinski

Laboratory for Analytical Bioinorganic and Environmental Chemistry, National Research Council of France (CNRS), Hélioparc, 2, av. Pr. Angot, F-64053 Pau, France

E-mail: ryszard.lobinski@univ-pau.fr

ICP MS continues to play an important role in metallomics-related research allowing the correlation of the metals and their species content in the tissues with genetic information and physiological status of living organisms. Attractive features of ICP MS including its capacity for sensitive multielemental determination of metals and precise isotopic ratio measurements (in samples down to single cell size) allow drawing important conclusions in plant, animal and human physiology and disease diagnosis. In addition to bulk analysis, the coupling of ICP MS to laser ablation allows obtaining information on spatial distribution of elements and its isotopes within tissues with a resolution down to several μm.

The successful probing for trace metals and their species in biological systems, essential in metallomics, has been so far mostly carried out by inductively coupled plasma mass spectrometry (ICP MS) coupled to liquid chromatography or electrophoresis. However, the progress in electrospray ionisation Fourier transform mass spectrometry using electrostatic orbital trap (Orbitrap) and ion cyclotron resonance offers unparalleled resolution, accuracy of mass measurement, and intrascan dynamic range for the analysis of biomolecules. The coupling of HPLC – Orbitrap MS allows the detection of the heteroatom-isotopic pattern in mass spectra with the low- and sub-ppm mass accuracy regardless of the concentration. The rate of progress in the development of electrospray MS is likely to reduce the role of ICP MS in metallometabolomics and metalloproteomics. Nevertheless, this technique will still play an important role in careful optimisation of analytical protocols in order to eliminate (or at least to account for) the formation of artefact metal complexes during chromatography and electrospray ionisation.

The presentation discusses the state-of-the-art ICP MS in multielemental and multiisotopic analysis, elemental imaging and its complementarity with electrospray FT MS for the detection and identification of metal-complexes in biological samples. It will highlight the limitations and advantages of both techniques and present the conclusions on the perspectives of the use of ICP MS in metallomics. They will be illustrated by a number of case studies focused on current metalomics projects carried out at the Laboratory of the Analytical Bio-Inorganic Analytical and Environmental Chemistry in Pau, France.

References

[1] S. Mounicou, J. Szpunar and R. Lobinski, *Chem. Soc. Rev.*, 38 (2009) 1119-1138.

Wide-scope screening of polar emerging contaminants in environmental samples by HILIC-QToF-HR-MS/MS

A.A. Bletsou, A.A. Markatis, P. Gago Ferrero, N.S. Thomaidis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, Panepistimiopolis Zographou, 15771 Athens, Greece

E-Mail: ntho@chem.uoa.gr

TU01

Hydrophilic interaction liquid chromatography (HILIC) has been a valuable complementary technique to the reversed-phase liquid chromatography (RP-LC). Moreover, the combination to mass spectrometric detection may lead to increased sensitivity, due to enhanced ionization. High resolution mass spectrometry (HRMS) is providing additional identification points to a wide-scope screening of emerging pollutants in the environment. In this study, an HILIC-QToF-MS/MS method was developed, optimized and validated for the determination of polar and semi-polar emerging pollutants in environmental samples. The stationary and mobile phases were optimized, together with the composition of the in-vial solvents and the ESI parameters. Chromatographic separation was finally performed with an ACQUITY UPLC BEH Amide column and the sample analysis was carried out in both positive and negative ionization mode, through broad-band Collision Induced Dissociation (bbCID) mode, providing MS and MS/MS spectra, simultaneously. The method was applied in influent and effluent wastewater samples from the wastewater treatment plant (WWTP) of Athens. Sample preparation consisted of a mixed mode solid-phase extraction (SPE) step and reconstitution of the extract in the optimum conditions. Identification parameters were gathered for each analyte in a constantly–growing database, containing information over the retention time, parent ions and adducts, as well as fragment ions and ratios. Up to now, 685 emerging pollutants (EPs) and transformation products (TPs) including, among others, pharmaceuticals, illicit drugs, personal care products, pesticides, industrial chemicals and sweeteners are included in the database. A HILIC-HR-MS method constitutes a valuable approach for the determination mainly of polar compounds during screening of wastewater samples. Moreover, it can be an excellent supplementary technique to RP-HR-MS screening methods, by giving additional identification points. Such orthogonal verification of the analytes, positively found in the samples, was evaluated.

Acknowledgments

This research has been co-financed by the European Union and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) – ARISTEIA 624 (TREMEPOL project).

Advanced GCMSMS analysis using a novel ionization technology and qTOF mass analyzer

A.A. Bisi, B.M.C. Salvi and C.A. Patkin

[1]PerkinElmer Italia Viale Innovazione 3 Milano (It)
[2]PerkinElmer, Bridgeport Av. Shelton CT (US)

E-mail: Ariovaldo.bisi@perkinelmer.com

Gaschromatography coupled to tandem mass spectrometry detection is today the first choice for the analysis of volatiles and semi-volatiles contaminants in environmental protection and food safety applications because of the high sensitivity and selectivity provided by MSMS analyser based on triple-quadrupole technology and electron impact ionization.
To substantially improve the quality of analysis we adopted a novel ion source based on a different approach to Electron Impact technology called Cold EI and qTOF analyser geometry:

- In standard 70 eV EI we observe that intensity of molecular ion is decreasing with the molecular weight; this behaviour reduces the ability to assign the proper MW to homologues and lowers the sensitivity in MRM acquisition. Cold EI provides stronger intensity molecular ions compared to standard EI improving the detection and identification of high MW and labile products.
- TOF analyser has a much faster acquisition speed vs. quadrupoles and, if properly designed, has also good sensitivity and linearity. A MSMS analyser based on qTOF geometry can improve qualitative information providing the full mass spectrum instead of MRM.

The lecture will cover basics of instrumental technology and report analytical data of analysis in several application fields with specific focus on hydrocarbons, environmental and biological fluids.

Volatile compounds of some aromatic plants of Algerian semi-arid' area by (HS-SPME) coupled to (GC/MS)

A. Bouguerra[1], Th. Massouras[2], N. Zouaoui[1] and M. Barkat[1]

[1]BIOQUAL laboratory, I.N.A.T.A.A, Mentouri Brother's Univerity,
Ain El Bey, Constantine, Algeria
[2]Department of Food Science and Human Nutrition, Laboratory of Dairy Science and Technology,
Agricultural University of Athens, Iera odos 75, 11855 Athens, Greece

E-mail: theomas@aua.gr

TU03

The aromatic plants with their diversities in the regions arid and semi-arid constitute an immense reservoir of new potential compounds, thanks to its molecules which have the advantage of a great diversity of chemical structure. In this context, the aim of the present study was the analysis of volatile compounds (VCs) released from the leaves and flowers of (13) thirteen Algerian aromatic plants. These plants are very abundant in the pasture of semi-arid areas of the east Algerian. The chemical composition of the volatile compounds (VCs) released from these herbs was investigated using Headspace Solid-Phase MicroExtraction (HS-SPME) coupled to Gas Chromatography /Mass Spectrometry (GC/MS). All tested aromatic plants (*Thymus algeriensis*, *Artemisia herba alba Asso*, *Rosmarinus officinalis* L., *Juniperus phoenica* L., *Marrubiumvulgare* L. and *Teucrium polium*) exhaled more than 150 different volatile compounds. Among those, camphor, camphene, α-pinene, 1, 8-cineole, Germacrene D, and trans-Caryophyllene, were the most abundant volatile components. The volatile compounds tentatively identified included alcohols, esters, carbonyl compounds and terpenes. *Rosmarinus officinalis* L. was caracterised by the presence of 1,8-Cineole, α-Thujone, β-thujone, Camphor, Germacrene D, Naphthalene, Camphene, and trans-Caryophyllene. *Thymus algeriens* was characterized by the presence of a group of alcohols particularly trans-geraniol, hexanol, benzylalcohol, Farnesol, hexanol and aganuspinol. However, the nature and level of the volatiles were notably varied and depending, region and part of the plant. Our results have conclusively demonstrated that the herbs of semi-arid areas of Algeria are rich volatile compounds (VCs). Consequently, HS-SPME/GC/MS, fast and simple method can be used for the analysis of the volatile compounds emitted from the aromatic plants.

Keywords: HS-SPME, GC/MS, aromatic plants, volatile compounds (VCs), semi-arid area

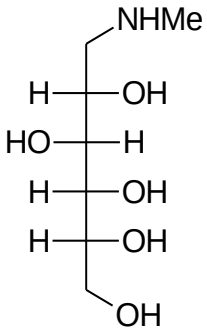
Impurity profiling of meglumine by HPLC-MS

F. Ferretti, C. Martano and L. Lattuada

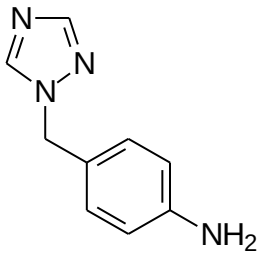
Bracco Imaging SpA, Bracco Research Center, Via Ribes 5, Colleretto Giacosa (TO), Italy

E-mail: fulvio.ferretti@bracco.com

N-Methyl-D-glucamine or meglumine **1** [1] is a secondary amine obtained from glucose and widely used as counter-ion in several pharmaceutical formulations especially when the needed concentration reaches values so high that sodium is no more a suitable choice.
An analytical method to assess the by-products profile of meglumine in a single HPLC run with MS detection is here described.
Since this compound, and its by-products, do not have chromophoric groups, MS spectrometry is an optimal way to detect and recognize the molecular structure of the components at the same time.
A commercial lot of meglumine was easily dissolved in milliQ water and the *N*-containing by-products (*e.g.* D-glucamine; *N*,*N*-dimethyl-D-glucamine) were separated using a strong cation exchange column (Agilent Zorbax 300 SCX 250x4.6 mm; 5 µm) with an acidic mobile phase (ammonium formate, 1g/L, and formic acid to correct pH at 2.6).
Moreover, in order to detect the possible occurrence of traces of glucose, meglumine was treated with a derivatizing agent that specifically reacts with carbonyl compounds. We found that commercially available 1-(4-aminobenzyl)-1,2,4-triazole **2** was the best choice because, turning glucose into a cation, strongly improved separation from other analytes in the HPLC run.
The proposed method has a considerable relevance in the pharmaceutical production as allows to check in a simple and reproducible way the level of reactive by-products that may condense with other ingredients, altering the final composition of the pharmaceutical formulations.



1



2

References

[1] *Merck Index*, 15th Edition (2013) 6150.

NMR spin- chromatography in dairy lipid research

C. Papaemmanouil[1], S. Symeou[5], C.G. Tsiafoulis[2,3], D. Alivertis[4], O. Tzamaloukas[5], D. Miltiadou[5], A.G. Tzakos[1], and I.P. Gerothanassis[1]

[1]Section of Organic Chemistry and Biochemistry, Department of Chemistry, [2]NMR Center,
[3]Laboratory of Analytical Chemistry, Department of Chemistry
[4]Department of Biological Applications and Technology; University of Ioannina, Ioannina GR-451 10, Greece
[5]Department of Agricultural Sciences, Biotechnology and Food Sciences, Cyprus University of Technology, P. O. Box 50329, Limassol 3603, Cyprus

E-mail: igeroth@uoi.gr

TU05

A rapid, direct and unequivocal spin-chromatographic separation and identification of minor components in the lipid fraction of common dairy products milk and cheese with the use of selective 1D TOCSY NMR experiments is presented [1]. The method was optimized with respect to the selectivity of the excitation pulse, the magnetization transfer rate and the relaxation properties of the lipid components. The spin chromatography method allows the complete backbone spin-coupling network to be elucidated even when present in strongly overlapped regions of the spectra and in the coexistence of major components such as triglycerides with $4x10^2$ to $3x10^3$ bigger NMR signal intensities. The proposed spin chromatography method, which does not require any derivatization steps for the lipid fraction, has been applied in the case of several compounds of interest e.g. conjugated linoleic acids, caproleic acid, linolenic and linoleic acids, DAG and MAG. Furthermore, it is selective with excellent resolution, sensitive, with quantification capability and compares favorably with 2D TOCSY [2], 2D DOSY and GC-MS methods of analysis [3]. The results of the present study demonstrate that the 1D TOCSY NMR spin-chromatography method can become a procedure of primary interest in food analysis and metabolomics [3].

References

[1] P. Sandusky and D. Raftery, *Anal. Chem.*, 77 (**2005**) 2455-2463.
[2] C.G. Tsiafoulis, T. Skarlas, O. Tzamaloukas, D. Miltiadou and I.P. Gerothanassis, *Anal. Chim. Acta*, 821 (**2014**) 62–71.
[3] C. Papaemmanouil, C.G. Tsiafoulis, D. Alivertis, O. Tzamaloukas, D.Miltiadou, A. Tzakos and I.P. Gerothanassis, **2015**, submitted.

Design Characteristics of a Post-Column Derivatization System for Tetradotoxin Analysis

D. Tanis, P. Vareltzis, G. Nikolaides and P.G. Rigas

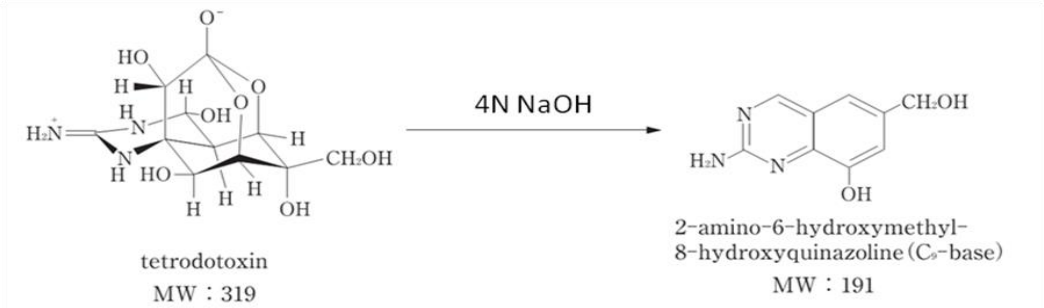
Alexander Technological Educational Institute of Thessaloniki, Department of Food Technology, Sindos 57 400, Greece

E-mail: rigas@aqua.teithe.gr

TU06

There has been a great interest in the use of high-performance liquid chromatography (HPLC) using post-column derivatization for improving detection selectivity or sensitivity. On-line, post-column derivatization offers a number of advantages over other possible derivatization approaches, but the possibility of band broadening in the post-column reactor must always be a concern. The choice of post-column reaction coil design is generally dictated by the reaction time required: Both coiled and knitted open tubular reactors were studied. The principles for improvements in radial mixing in open tubular reactors have been exploited both for coiled and knitted open tubular reactors also known as a three-dimensional coiled tube, The performances of these reactors are compared to coiled and knitted open tubes, using plate height vs. linear velocity (h vs. u) plots and calculations of relative band broadening.

The design of a post-column fluorescence derivatization system for the analysis of tetradotoxin is discussed theoretically and investigated experimentally. The chromatographic system involves the use of perfluorocarboxylic acids for the separation of tetrodotoxin and the derivatization reaction studied for the fluorescence detection of tetradotoxin is listed below:



Rules for optimal design are given for coiled and knitted tubular reactors. Theoretical investigation of the reactor design allows prediction of the general rules for the system optimization. Experimental studies involve the parameters which affect both the chromatographic band broadening and the sensitivity of the derivatization reaction.

References

[1] Carl M. Selavka, Kai-Sheng Jiao, and Ira S. Krull, Anal. Chem. 59(1987), 2221-2224.
[2] Chih-Yu Chen1 and Hong-Nong Chou, Acta Zoologica Taiwanica, 9(1) (1998),41-48.
[3] Kurt Hoffmsnn and lstván Halaz, J. Ckrornatogr., 173(1979), 211-228.
[4] Takeshi Yasumoto and Michishita Tooru, Agric. Biol. Chem. 49 (1985), 3077–3080.

.

Tuesday 22 September 2015

Royal Cruise Hall-D

Chair: A. Sanz-Medel, N. Kallithrakas

Mass Spectrometry/ Chromatography 2

HPLC profiles of phenolic compounds present in olive oil by-products extracts

S. Chanioti, P. Siamandoura and C. Tzia

Laboratory of Food Chemistry and Technology, School of Chemical Engineering, National Technical University of Athens, 5 Iroon Polytechniou St., 15780, Athens, Greece

E-mail: schanioti@gmail.com, psiamandoura@hotmail.com, tzia@chemeng.ntua.gr

The major olive oil by-products, olive kernel and olive leaves, contain significant amounts of polyphenolic compounds that provide health benefits including antioxidants and anti-inflammatory functions. In this study, different extraction techniques have been used to extract bioactives from olive leaves and olive kernel; among them, conventional extraction with ethanol: water. New-types of extraction technique, microwave-assisted extraction (MAE) and enzyme-assisted extraction (EAE) were used in order to investigate their feasibility on the extraction of polyphenols from olive kernel and leaves. These modern extraction techniques can be regarded as a possible tool not only from a laboratory point of view but also for food industries. To our knowledge, the combined use of enzymes and microwave-assisted extraction of polyphenols from olive kernel and leaves has not been previously reported. An enzyme cocktail comprised of pectinase and polygalacturonase was used. The phenolic compound of the different extracts were studied and quantified by HPLC-DAD. The results showed that the different extracts had different phenolic profiles (including hydroxytyrosol, oleuropein, tyrosol, caffeic acid, vanillin, rutin and lutein) in different amounts. The antioxidant potential of extracts prepared from olive kernel and leaves in terms of their total phenolic is evaluated. The results varied depending on the extraction methods and therefore they may be helpful to further exploit and utilize these resources.

Investigation of the Cr(VI) behavior in foods by HPLC – ICP MS

V. Vacchina, I. de la Calle and F. Séby

UT2A, Pau, France

E-mail: veronique.vacchina@univ-pau.fr

TU08

Chromium is an element that exists under two oxidation states, Cr(III) and Cr(VI). Whereas Cr(III) is essential to life, Cr(VI) is considered carcinogenic. Cr(VI) speciation is now performed in routine for environmental samples (water, soils…) by HPLC – ICP MS. However it is much more difficult to achieve in foods due to extraction problems, carbon interferences and the lack of knowledge on the behavior of the chromium linked with the matrix. The objective of our work was therefore twofold :

- to investigate the reactions occurring between Cr(VI) and the food matrices
- to develop a specific and sensitive analytical method for Cr(VI) quantification in such samples.

Different kinds of samples have been investigated like milk and dairy products, fruits and vegetables, fish, meat, etc… The presentation will display firstly the interactions between Cr(VI) and the different matrices investigated (by size-exclusion HPLC – ICP MS). The method developed for the specific Cr(VI) measurement by ion-exchange HPLC – ICP MS will then be detailed in terms of analytical development, validation criteria obtained in the absence of Certified Reference Material and its application for the determination of Cr(VI) in a wide range of products from a local supermarket. Finally, the method developed has been applied to study the stability of Cr(VI) in milk over storage and cooking.

The use of immobilized artificial membrane chromatography for modelling bioconcentration of pharmaceutical compounds in the environment

F. Tsopelas[1], C. Stergiopoulos[1], A. Tsantili- Kakoulidou[2] and M. Ochsenkühn-Petropoulou[1]

[1]Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, 157 80 Athens, Greece
[2] Laboratory of Pharmaceutical Chemistry, School of Pharmacy, University of Athens, Panepistimiopolis, Zografou, 157 71 Athens, Greece

E-mail: ftsop@central.ntua.gr

Bioconcentration is a property of paramount importance in environmental sciences, considered as a measure of the accumulation of xenobiotics in the trophic chain due to dietary absorption. The main physicochemical property influencing to a large extent the environmental fate of chemicals in the environment as well as their bioaccumulation tendency is lipophilicity, expressing as the logarithm of octanol-water partition or distribution coefficient (logP or logD). The traditional measurement of the determination of octanol- water partitioning is a time-consuming technique, not applicable for compounds undergoing degradation. Liquid chromatography offers a popular alternative for measuring lipophilicity, providing rapid measurements. Especially, Immobilized Artificial Membrane Chromatography (IAM) has been used for the investigation of the interactions between membranes and pharmaceutical compounds and the prediction of human intestinal absorption and CNS permeation. However, its application to environmental sciences for the evaluation of bioaccumulation tendency of chemicals is still missing.

In the present work, the retention of a set of structurally- diverse pharmaceutical compounds was studied on an IAM stationary phase, IAM.PC.MG type. Retention was expressed as the logarithm of the retention factor measured or extrapolated to 100% aqueous phase ($\log k_w$). The results were combined with previous data obtained under the same conditions in order to establish relationships with bioconcentration factors, collected by the literature. As additional physicochemical parameters, molecular weight, Abraham's hydrogen- bond acidity and basicity parameter, topological polar surface area as well as positively and negatively charged molecular fractions were tested. The obtained relationships were compared with those derived by replacing IAM retention factor with octanol-water partitioning, expressed as logD.

References

[1] F. Tsopelas, N. Malaki, T. Vallianatou, M. Chrysanthakopoulos, D. Vrakas, M. Ochsenkühn-Petropoulou and A. Tsantili- Kakoulidou, *Journal of Chromatography A*, 1396 (2015) 25-33.
[2] F. Tsopelas, A. Tsantili- Kakoulidou and M. Ochsenkühn- Petropoulou, *Microchemical Journal*, 110 (2013) 711-718.
[3] F. Tsopelas, M. Ochsenkühn- Petropoulou, A. Tsantili- Kakoulidou and K.M. Ochsenkühn, *Analytical and Bioanalytical Chemistry*, 381 (2005) 420-426.

Multianalyte assay for prostate cancer-related gene quantification by hybridization on fluorescent microspheres

I.K. Kyriakou[1], K. Mavridis[2], D.P. Kalogianni[1], P.C. Ioannou[3], Th.K. Christopoulos[1], A. Scorilas[2]

[1]Department of Chemistry, University of Patras, Patras, Greece 26504
[2]Department of Biology, University of Athens, Athens, Greece 15771
[3]Department of Chemistry, University of Athens, Athens, Greece 15771

E-mail: tchrist@upatras.gr

TU10

Prostate cancer (PCa) is the second most common cancer in men and the fifth most common cancer overall. This fact necessitates early diagnosis, prognosis and monitoring of patients with prostate cancer. Consequently, there is a pressing demand for new sensitive and specific biomarkers. In this work, we developed a multiplex quantitative competitive polymerase chain reaction (QC-PCR) assay for simultaneous determination of 7 mRNA transcripts of PCa-related genes, including 5 genes from the kallikrein family (KLK3, KLK4, KLK5, KLK11 and KLK15), the prostate-specific membrane antigen (PSMA) and prostate cancer 3 (PCA3). In addition, the HPRT1 mRNA was quantified as a housekeeping gene. Isolated RNA from cell lines and clinical samples was first reverse transcribed followed by the addition of 8 synthetic DNA internal standards (DNA competitors) at a level of 5000 copies of each. DNA competitors had the same size with their respective targets, differing only in a 24-bp segment located in the middle of their sequence, thus allowing subsequent discrimination by hybridization. The addition of competitors allowed compensation for any variation of PCR efficiency. After amplification by multiplex PCR, the products were thermally denatured and hybridized with specific oligonucleotide probes immobilized on the surface of spectrally encoded fluorescent microspheres. All 16 DNA amplification products were biotinylated at the 5' end through biotin-modified primers. The hybrids were detected by using a streptavidin-phycoerythrin conjugate via streptavidin-biotin interaction. Finally, the microspheres were analyzed by flow-cytometry employing two laser beams. The first laser beam was used for the classification of microspheres into groups, thereby identifying the corresponding gene, while the second laser beam was used for the excitation of phycoerythrin, whose fluorescence was directly related to target concentration. We performed calibration graphs for the 16 PCR products demonstrating analytical ranges from 10 to 1000 pM. Extensive cross-hybridization assays were carried out, in which each target was hybridized separately with a pool of all 16 probes. These experiments proved the specificity of the assay.

Acknowledgements: This research has been co-financed by the European Union (European Social Fund - ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALES, investing in knowledge society through the European Social Fund (UoA-BIOPROMO, MIS 377046).

The comparison of Capillary Electrophoresis and Ion Chromatography with Electrospray Ionization-Mass Spectrometry methods for thermal stability studies on ionic liquids

M. Pyschik, M. Winter and S. Nowak

University of Muenster, MEET Battery Research-Center, Corrensstraße 46, 48149 Muenster, Germany

E-mail: marcelina.pyschik@uni-muenster.de, sascha.nowak@uni-muenster.de

In the last years, ionic liquids (ILs) gained more and more attention for different chemical applications as for example effective solvents, catalysts for chemical reactions or as electrolyte in lithium-ion batteries. The application fields are widely spread, therefore ILs need to meet different requirements. But the most important requirement for all application fields is the thermal stability of ILs. So far, the degradation of ILs are usually investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) or theoretical calculations [1]. However, only few researchers investigated the degradation products via chromatographic methods, like Zhou *et al.*, which used high-performance liquid chromatography (RP-HPLC) with a monolithic column for the determination of BF_4^- in ILs [2].
We have developed and optimized in our research group new ion chromatography (IC) and capillary electrophoresis (CE) methods hyphenated to an ESI-MS system to analyze and identify cation and anion degradation products of different ILs [3]. The investigated ILs are pyrrolidinium- and imidazolium- based. The IC and CE was hyphenated to ESI-MS to identify various unknown degradation compounds, which were not mentioned in the literature before. The degradation products can be separate from each other and can be quantified to ascertain degradation processes (Figure 1).

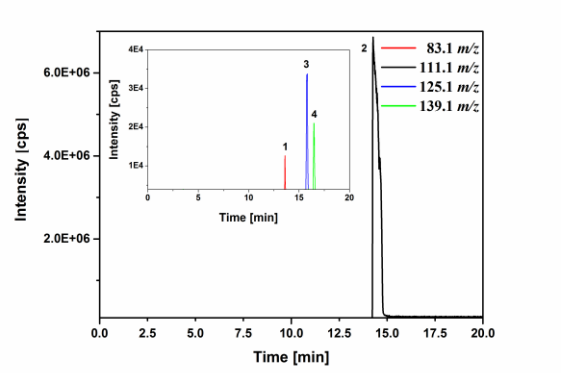


Fig. 1: Imdiazolium-based IL and the degradation products measured by CE/ESI-MS.

References

[1] S.D. Chambreau, J.A. Boatz, G.L. Vaghjiani, C. Koh, O. Kostko, A. Golan and S.R. Leone, *J. Phys. Chem. A*, 116 (2012) 5867-5876.
[2] S. Zhou, H. Yu, L. Yang and L. Ai, *J. Chrom. A*, 1206 (2008) 200-203.
[3] M. Pyschik, V. Kraft, S. Passerini, M. Winter and S. Nowak, *Electrochim. Acta*, 130 (2014) 426-430.

Conformational Characterization of Polyelectrolyte Complexes Using Ion Mobility-Mass Spectrometry

M. Atakay[1], Ch. Wesdemiotis[2] and B. Salih[1]

[1]Hacettepe University, Department of Chemistry, 06800 Ankara/TURKEY
[2]The University of Akron, Department of Chemistry, Akron, OH 44325-3601, USA

E-mail: bekir@hacettepe.edu.tr

TU12

Mass spectrometry is the most convenient technique for obtaining useful information about the formation parameters of non-covalent complexes in both solution and gas phases with high accuracy and sensitivity. Ion mobility mass spectrometry (IM-MS) also gives size and shape information of an ion in addition to its mass-to-charge ratio and fragmentation pathway data. This technique has been used to determine the conformations of polymers [1] or biomolecules such as peptides, and proteins [2,3]. Collision cross sections of ions can be determined using drift time data of ions in ion mobility cell that is directly depend on the size and shape of the ions. Experimental cross sections of standard samples are used for obtaining the details of the conformations of ions. In our studies, we have investigated the conformational and stability features of polyelectrolyte complex ions in gas phase using IM-MS. Polyelectrolytes are molecules comprised of a large number of functional groups that are charged or could become charged under certain circumstances. They have been commonly used as functional agents for the modification of inert material surfaces. Polyanions and polycations can be added to a surface in an alternating pattern via electrostatic interactions. Polyelectrolyte multilayers are formed on material surfaces via this layer-by-layer method create biocompatible surfaces. Polyelectrolyte layers have the ability to interact with charged biomolecules and, therefore, are used in various biomedical and chemical sensor applications, tissue engineering, and drug delivery system. In our studies, the collision cross-sections of non-covalent polyelectrolyte complex ions are derived separately for comparing their compactness in gas phase. The data obtained from mass spectrometric studies reveal insight about the potential performance of such ions in polyelectrolyte multilayer films in the solution phase. The stabilities and conformations of polyelectrolyte complexes affect their ability to capture biomolecules or drugs, and they are also important for understanding how polyelectrolyte films react when in contact with biological media in vivo.

References

[1] D. Morsa, T. Defize, D. Dehareng, C. Jerome, and E. De Pauw, *Analytical Chemistry*, 86 (2014) 9693−9700.
[2] M. Khakinejad, S. G. Kondalaji, H. Maleki, J. R. Arndt, G. C. Donohoe, S. J. Valentine, *Journal of The American Society for Mass Spectrometry*, 25 (2014) 2103-2115.
[3] B. T. Ruotolo, J. L. P. Benesch, A. M. Sandercock, S. Hyung, C. V. Robinson, *Nature Protocols*, 3 (2008) 1139 - 1152.

Tuesday 22 September 2015

Royal Cruise Hall-A

Chair: J. Szpunar, N. Thomaidis

Mass Spectrometry

Invited lecture

Novel Plasma-MS instrumentation for P- and S- guided targeted proteomics and nm-scale depth-profile solid analysis

S. Diez Fernández, J. Ruiz Encinar and A. Sanz-Medel

Department of Physical and Analytical Chemistry, University of Oviedo, 33006 Oviedo, Spain

E-mail: asm@uniovi.es

IL12

Research carried out previously in our laboratory demonstrated that ICP-MS can play a key role as a complementary MS-based detector for absolute determinations in metalloproteomics. Traditionally, however, the non-metals S and P have been considered "not-so-good" elements for ICP-MS detection, in spite of their outstanding interest in biomedicine, particularly in proteins and peptides. The introduction two years ago of a new instrument, the ICP-tandem-MS or ICP-(Q,Q,Q)MS detector is changing the scene because it provides two levels of selectivity via an appropriate gas reaction in the reaction cell located between the first and last MS analysers. The instrument enables the simultaneous analysis of S and P at extremely low detection limits (e.g 3 orders of magnitude more sensitive for P [1] than the expensive ICP-double focusing- High Resolution MS analysers). This feature is opening new avenues in targeted absolute quantitative proteomics by using capLC-ICP-MS(Q,Q,Q) and 34S isotope dilution analysis. Also, new departures of using this instrument for global and site-specific direct determinations of proteins phosphorylation and their potential as early alarm biomarkers of skin cancer will be addressed.

A quite different plasma-MS instrumental development I would like to discuss today is the Pulsed Glow Discharge-Mass Spectrometer (PP-GDMS(TOF)), as developed in our laboratory [2]. Two important analytical applications (elemental depth profiling of nm-layered materials and elemental/molecular screening of polymeric materials) will be demonstrated, the first one to depth profile analysis in amorphous silicon thin film solar cells and the second to analyse layered thin-film composite membranes and investigate their resistance to corrosion by using the modern PP-GDMS(TOF) tool [3]. At this moment the first worldwide commercial PP-GDMS(TOF) is available in our Analytical Spectrometry Group in Oviedo [4]. Thus, we will discuss its analytical potential for direct bulk analysis of solid materials and depth profile analysis in thin films with nanometric depth resolution.

References

[1] S. Diez Fernández, N. Sugishama, J. Ruiz Encinar and A. Sanz-Medel, *Anal. Chem.*, 84 (2012) 5851−5857.

[2] A. Solà-Vázquez, B. Fernández, J.M. Costa-Fernández, R. Pereiro and A. Sanz-Medel, *Anal Bioanal Chem.*, 29 (2013) 7431-7443.

[3] A. Alvarez-Toral, P. Sanchez, A. Menéndez, R. Pereiro, A. Sanz-Medel, and B. Fernández. *J. Am. Soc. Mass Spectrom.*, 26 (2015) 305-314.

[4] http://www.unioviedo.es/analyticalspectrometry/news.

Using Ambient Mass Spectrometry source for the analysis of nanometer thick organic layers in nanoparticle

A.A. Bisi[1], and S. Reddy[2]

[1]PerkinElmer Italia Viale Innovazione 3 Milano (It)
[2]PerkinElmer, Bridgeport Av. Shelton CT (US)

E-mail: Ariovaldo.bisi@perkinelmer.com

TU13

Capped nanoparticles structure is formed by an inner solid core, usually a metal, and a polymeric coating to be used as support for active molecules like therapeutics, permeation enhancers and targeting agents.
The analysis of number and size of the nanoparticles is accomplished using last generation ICP-MS and preliminary separation techniques like Field Fractioning.
To analyze the organic layer is absolutely challenging because of the very thin layer of polymer coating the sold core. A viable approach is to use Ambient Mass Spectrometry with Direct Sampling Analysis (DSA) source coupled to a high-resolution, exact mass Time of Flight analyzer and in this oral presentation we'll discuss the results obtained with direct analysis of samples without preliminary preparation.
Using ambient ionization DSA source with the high resolution accurate mass TOF mass spectrometer, we were able to characterize ligand capping of the Au nanoparticles:
Mass spectral analysis showed the BPEI ligand bound to Au through lipoic acid
Analysis of dodecanethiol capped ligands shows other impurities maybe bound to the particles including octadecane thiol
Semi quantitative analysis can be performed on ligand capped gold nanomaterials
Mixtures of ligands bound to nanoparticles can be identified and confirmed by AxION DSA/TOF
Conclusion:
Mass spectrometry is the most selective and specific detection tool available to identify the organic ligands bound to nanoparticles.
More specifically, the AxION DSA/TOF mass spectrometry allows for rapid identification and confirmation of these ligands without any elaborate sample preparation. Analysis can be done in seconds.
The AxION DSA/TOF along with powerful visualization software tools offers a rapid way to screen and confirm for ligands capping of nanoparticles.

.

Investigation of single-particle ICP-TOFMS as a tool for comprehensive sizing and counting of mixtures of engineered nanoparticles

A. Gundlach-Graham[1], A. Praetorius[2], J. Navratilova[2], B. Ramkorun-Schmidt[3], F. von der Kammer[2], and D. Günther[1]

[1] Laboratory of Inorganic Chemistry, ETH Zurich, Vladimir-Prelog-Weg 1, CH-8093 Zurich, Switzerland
[2] Department of Environmental Geosciences, University of Vienna, Althanstraße 14, 1090 Vienna, Austria
[3] BAM Federal Institute for Materials Research and Testing, Richard-Willstätter Str. 11, 12489, Berlin, Germany

E-mail: agraham@ethz.ch

Single-particle inductively coupled plasma mass spectrometry (sp-ICPMS) is quickly maturing into a routine analytical method for the sizing and counting of metallic nanoparticles (NPs). In sp-ICPMS, a dilute suspension of NPs is introduced into the ICPMS instrument, and ion signal is recorded with enough time resolution to separate discrete ion signals from each NP event. The structure and frequency of these sp-ICPMS signals carry information about the NP suspension, including particle-number concentration (PNC) and particle size. Importantly, ICPMS presents a route to measure very low (environmentally relevant) PNCs because the measured analytical signal does not depend on total mass concentration, but on the size of each NP: to detect many NPs in low-PNC samples, one only has to wait long enough.

Despite the attractive measurement characteristics offered by sp-ICPMS, current implementations of sp-ICPMS with conventional ICPMS instrumentation are limited. In particular, quadrupole and sector-field MS (QMS and SFMS) instruments can only be used to measure one isotope within the time scale of transient NP signals (200-500 µs); therefore, sp-ICPMS experiments are limited to measurement of a single isotope. In addition, current sp-ICPMS approaches rely on the use of external NP standards for calibration of NP sizes and PNCs; this limits application because accepted NP standards are scarce and because sp-ICPMS can currently only be applied in a targeted manner, with prior knowledge of the NPs of interest.

In this presentation, we report current developments of ICP-time-of-flight mass spectrometry (ICP-TOFMS**)** for the analysis of engineered NPs from complex matrices. ICP-TOFMS provides simultaneous, complete-isotope detection at spectral-generation rates up to 33 kHz, and provides sensitivities that rival QMS and SFMS for NP detection. The fast, multi-isotope detection provided by ICP-TOFMS enables the development of new NP-detection strategies for more complete characterization of NP suspensions. By combining standard pneumatic-nebulization sample introduction with discrete-droplet introduction of standard solutions, we demonstrate a method for online size calibration and instrument-drift correction for the analysis of multi-element mixtures of NPs. In addition, we report how simultaneous multi-isotope detection enables the identification and discrimination of naturally occurring versus engineered CeO_2 NPs in soil samples.

Development of isolation of psychoactive compounds from plants using the microwave- and ultrasound-assisted extraction techniques

M. Woźniakiewicz[1], J. Nowak[1], M. Ciechomska[1], A. Woźniakiewicz[1] and P. Kościelniak[1]

[1]Laboratory for Forensic Chemistry, Faculty of Chemistry, Jagiellonian University in Kraków, Ingardena 3, 30-060 Kraków, Poland

E-mail: michal.wozniakiewicz@uj.edu.pl

TU15

Determination of psychoactive compounds in plant material is frequently crucial in forensic investigation as their concentration is usually divergent in each plant organ. Moreover, they may vary between plants of the same genus cultivated in different conditions, implying diverse symptoms after being ingested by human beings. One of the most essential step in the analytical procedure for plant material investigation is a proper extraction method enabling complete transfer of analytes to the liquid medium. Another problem is the extracts purification, enhancing chromatographic separation and preventing matrix effects in mass spectrometry detection, caused mainly by lipids and chlorophyll presence.

In the presented work, organs of plants from *Solanaceae* Juss. family (*Datura* L. and *Brugmansia* Pers.) and from *Ipomoea* L. genus containing tropane alkaloids (atropine and scopolamine) and ergot alkaloids (ergine, ergometrine), respectively, were analyzed. Atropine and scopolamine as anticholinergic agents cause among others: dryness of mouth, anxiety, tachycardia, delirium, euphoria and hallucinations, whereas ergot alkaloids, mostly ergine, can induce LSD-like effects [1,2]. Methods of extraction, including microwave-assisted extraction (MAE), and ultrasonic-assisted extraction (UAE) were developed and optimized for processing of leaves and seeds. Then, the samples were analyzed by GC-MS and LC-MS methods for tropane alkaloids and ergot alkaloids determination, correspondingly.

It was found that MAE with methanol as the extraction solvent, followed by BSTFA/TMCS derivatization to enhance the GC-MS analysis, was the most suitable for *Solanaceae* samples. In contrary, for *Ipomoea*, MAE was found to be too aggressive, so destructive for analytes, therefore UAE in methanol/water was utilized. In both cases, the complete efficiency of the extraction was achieved. Then, the extracts purification procedures with graphitized carbon black, PSA, Chlorofiltr® and Z-sep® sorbents were evaluated. The validated methods were successfully applied for analysis of *Datura metel* L. leaves and seeds, *Brugmansia pittieri* (Saff.) Moldenke leaves and Morning Glory seeds and leaves from Heavenly Blue cultivar.

References

[1] J.E. Ketchum, F.R. Sidell, E.B. Crowell Jr, G.K. Aghajanian and A.H. Hayes Jr, *Psychopharmacologia*, 28 (1973) 121-145.

[2] A. Paulke, C. Kremer, C. Wunder, M. Wurglics, M. Schubert-Zsilavecz, and S.W. Toennes, *Forensic Sci. Int.*, 242 (2014), 62–71.

Wide-scope QSRR models to support suspect and non-target screening of polar compounds in HILIC - ESI(+) - LC-HRMS

R. Aalizadeh and N.S. Thomaidis

Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

E-mail: ntho@chem.uoa.gr

The aquatic environment has been increasingly challenged by the continuous use and discharge of polar compounds, like new generation of pesticides, pharmaceuticals, illicit and new psychoactive drugs and their transformation products or metabolites. Therefore, robust and fast methods with large applicability domain are required to identify these compounds in environmental samples. Nowadays, liquid chromatography coupled with high resolution mass spectroscopy plays a significant role for the identification of polar and mid-polar compounds. Hydrophilic interaction chromatography (HILIC) is an alternative separation technique that is used increasingly for their identification by liquid chromatography – high resolution mass spectrometry (LC-HRMS). However, well-established retention time prediction models with wide applicability domain have not been presented so far to support suspect and non-target HRMS screening of samples. In this work, a large dataset consisted of 685 polar compounds were analyzed by HILIC-LC-QToFMS, and their retention time in positive electrospray ionization mode were derived. Quantitative structure-retention time method was used to correlate their chemical structures with the observed retention times. The molecular descriptors were generated using Dragon and Marvin software, and then, the prepared dataset was split into training and test set based on principle components analysis and k-medoids clustering technique. Genetic algorithm was used for selecting the relative molecular descriptors among the generated variables. After selection of relevant group of descriptors, Kohonen Self-Organizing Maps (SOMs) was used to evaluate the accuracy of classification and also selection. Multiple linear regression (MLR) and support vector machine (SVM) were used as regression tools and then validated by several validation techniques. The applicability domain of the proposed models was studied carefully by a new display of Williams plot and Monte Carlo sampling method. The results indicated that LogD, AlogP, and maximum negative charge that a molecule can carry have major relative importance between modeling variables. This work provides the first, validated and robust model for estimating retention time of compounds in HILIC-LC-HRMS platforms for large number of polar compounds to improve their identification by suspect and non-target screening workflows.

Invited lecture

Combined speciation techniques proof changes in the metallome and metabolome as a cause for transition-metal related neurodegeneration

B. Michalke and K. Neth

Helmholtz-Center Munich - German Research Center for Environmental Health GmbH, Research Unit Analytical BioGeoChemistry, Ingolstädter Landstr. 1, 85764 Neuherberg, Germany

E-mail: bernhard.michalke@helmholtz-muenchen.de

Transition metals play a crucial role in proper brain function. Misbalances of various metal ions, occasionally induced by overexposure, are known to severely affect brain, resulting in neurodegeneration. As an example, chronic Manganese exposure leads to degeneration of dopaminergic neurons inducing a Parkinson-like complaint called Manganism. Deciphering uncontrolled transport across neural barriers (NB) and the ongoing neurodegenerative mechanisms in the affected brains is still a major task for understanding the complex modes of action.

First we analyzed and identified relevant Mn-carriers (Mn species) being responsible for a widely uncontrolled transport across neural barriers (NB): Mn speciation in paired serum/cerebrospinal fluid (CSF) samples was performed two-dimensionally by SEC-ICP-DRC-MS and CZE-ICP-DRC-MS. The most important Mn-carrier, Mn-citrate, was identified by ESI-FT-ICR-MS. Elevated Mn-citrate concentration in serum were shown to act as marker for increased Mn concentration in CSF (and brain), the latter elevating the risk of Mn-dependent neurological disorders.

Second, to clarify molecular mechanisms of Mn-neurotoxicity we applied SEC-ICP-DRC-MS for Mn-speciation and ESI-FT-ICR-MS and IC-ICP-OES to rat brain extracts after low-dose Mn-feeding, simulating chronic Mn-exposure. ESI-FT-ICR-MS-analysis of brain extracts revealed an increase in oxidative stress markers like glutathione-disulfide (GSSG), prostaglandins, and 15(S)-HETE, a marker for lipid peroxidation. Acetylcholinesterase activity and glutamate concentrations were also increased in brain samples of Mn-supplemented rats, indicating oxidative stress in brain, too. Furthermore, a shift in neuronal Fe(III) to Fe(II) was observed, promoting Fenton reaction and formation of chemical radicals. For the first time altered Fe-species distribution could be related to Mn-induced neuroinflammation, enlarging knowledge of this complex neurodegenerative condition. Additionally, up to several hundred metabolites were shifted under Mn exposure but not uniformly. Metabolites correlated either positively to specific Mn-species, and others negatively. The combination of various speciation- and different mass spectrometry techniques provided information how Mn enters the brain without efficient control at NB and provided substantial evidence that Mn-induced neuroinflammation leads to oxidative stress triggered by multifactorial pathophysiological processes.

Tuesday 22 September 2015

Royal Cruise Hall-B

Chair: M. Woźniakiewicz, R. Aalizadeh, Th. Lymperopoulou, C. Tsiafoulis

Poster Session 2

Mass Spectrometry

Chromatography

Two Temperature sorption strategy for screening of volatile compounds in barley and wheat malts by method based on solid phase microextraction

M. Adam, A. Eisner, K. Adámková, P. Bajerová and K. Ventura

University of Pardubice, Faculty of Chemical Technology, Department of Analytical Chemistry, Studentska 573, 532 10 Pardubice, Czech Republic

E-mail: Martin.Adam@upce.cz

P2-01

In this study, a modern sampling approach based on the use of two extraction temperatures in the same headspace solid-phase microextraction (HS-SPME) procedure was optimised and evaluated for the analysis of aromaprofile of barley and wheat malt samples. Separation and identification of target compounds was realised by gas chromatography–mass spectrometry (GC–MS) method. This modern sorption strategy is aiming at extracting a significantly higher number of compounds with wider range of volatilities comparing to conventions sorption strategy using only one sorption temperature [1, 2].

As an analytical tool, experimental designs were used for the method optimisation. First of all, the most significant factors affecting the whole procedure were evaluated by the approach based on the Plackett–Burman design. After that, the final experimental conditions were established by five-level orthogonal central composite design optimisation approach followed by response surfaces modelling.

The proposed method presents a very good compromise of conditions under which the right combination of sorption temperatures could achieve a much better extraction enabling identification of more volatile and semi-volatile compounds in obtained chromatograms.

This method was compared to conventional approach based on the sorption at a single extraction temperature. It was confirmed that the presented method provides a better results considering the response in terms of both the total peak areas and mainly the number of identified compounds. The use of two extraction temperatures in a single assay for the HS-SPME procedure proved to be a very good alternative for the screening of compounds present in barley and wheat malts with a wide range of volatilities.

References

[1] J.N. Bianchin, G.S. Nardini, J.O. Merib, A.N. Dias, E. Martendal and E. Carasek, *Food Chemistry*, 145 (2014) 1061–1065.

[2] G.S. Nardini, J.O. Merib, A.N. Dias, J.N.B. Dutra. C.D.S. Silveira. D. Budziak, E. Martendal and E. Carasek, *Microchemical Journal*, 109 (2013) 128–133.

A HPLC-MS/MS Method for the accurate quantification of Cyclopiazonic Acid using stable isotope as Internal Standard

P. Ansari and G. Häubl

Romer Labs Division Holding GmbH, Technopark 1, 3430 Tulln, Austria

E-mail: parisa.ansari@romerlabs.com

P2-02

Cyclopiazonic acid (CPA) is an indole tetramic acid mycotoxin with tremorgenic, neurochemical and mutagenic toxicity [1]. It is produced by certain *Penicillium* and *Aspergillus* spp. [2], including two important industrial molds for the production of fermented foods (*Penicillium camemberti* and *Aspergillus oryzae*) [3]. By consuming contaminated feed, the animals accumulate CPA in their muscles, milk and eggs and humans are exposed to CPA by ingesting these products, as well as by direct consumption of contaminated agricultural products. Therefore, it is important to have accurate analytical methods for the detection and quantification of CPA in food and feed [3][4].

We have developed and optimized an HPLC-MS/MS method for the detection and quantification of CPA in food and feed samples. To compensate the matrix effect in complex products and guarantee accurate quantification, fully carbon-13-labelled CPA was produced and used as internal standard (IS). To verify the applicability of this ^{13}C-labelled CPA as IS, several commercial available white mould cheese samples were tested with this method. The samples were extracted with 0.1% formic acid in acetonitrile. After centrifugation, the supernatant was spiked with the IS and directly injected into the HPLC-MS/MS, without any further clean-up or dilution step.

A validation of the developed method for the white mould cheese matrix showed an LOD of 0.2 µg/kg and an LOQ of 0.5 µg/kg. The recoveries of spiked cheese samples were around 90%. In some commercially available white mould cheeses, high amounts of CPA (up to 3800 µg/kg) could be found.

The 13C-labelled CPA as IS for an HPLC-MS method compensates matrix effects; therefore it is a good tool to get more reliable results. The presented method is applicable for detection of CPA in difficult food and feed matrices and does not need sophisticated clean-up.

References

[1] Y. Hayashi and T. Yoshizawa, *Food Chem.*, 93 (2005) 215–221

[2] J.W. Dorner, R.J. Cole, L.G. Lomax, H.S. Gosser and U.L. Diener, Appl. Environ. Microbiol., 46 (1983) 698-703

[3] T. Goto, E. Shinshi, K. Tanaka and M. Manabe, Agric. *Biol. Chem.*, 51 (1987) 2581–2582.

[4] R. Krska, J.L. Richard, R. Schuhmacher, A.B. Slate, and T.B. Whitaker, Guide to Mycotoxins (2012) 4th Edition, Romer Labs

Trace elements in beers from Greek microbreweries by ICP-MS

E. Bempi[1,2], S. Karavoltsos[1], A. Sakellari[1], A. Kaliora[2], E. Dassenakis[1] and N. Kalogeropoulos[2]

[1]National and Kapodistrian University of Athens, Department of Chemistry,Laboratory of Environmental Chemistry, Panepistimioupolis, 157 84 Athens, Greece
[2]Harokopio University,Department of Nutrition and Dietetics,Laboratory of Chemistry-Biochemistry-Physical Chemistry of Foods, 176 71 Athens, Greece

E-mail: el.bempi@gmail.com

P2-03

The trace elements content of beers is of interest as they can affect the products' quality including organoleptic characteristics andstability, while at the same time they are related to the health status of the consumers [1].
Towards this end, thirty one beers produced by Greek microbreweries were analysed for trace elements by inductively coupled plasma – massspectrometry (ICP-MS; Thermo Scientific ICAP Qc).
The samples were digested using concentratedHCl and $HClO_4$(1:1 v/v) by applying heat in closed PTFE vessels. All measurements werecarried out in a single collision cell mode, with kinetic energydiscrimination (KED) using pure He.
The elements determined were As, Cd, Co, Cr, Cs, Cu, Fe, Mn, Ni, Rb, Sr, and V. The higher median values - >550 μg/L- were found for Fe, followed by those for Rb and Mn which were determined at the range 100-200μg/L; Cu, Sr and V were at the range 10-100μg/L; As, Co and Cr were found at 1-10μg/L; finally, the median values for Cs, Cd and Ni were <1 μg/L.
By performing principal components analysis (PCA) of the data obtained for the 12 elements, 4 components were extracted, which together accounted for 72.1% of the variability in the original data; the metals tend to cluster together forming three groups of elements comprised by (i) Co, Fe, Mn, Ni (ii) Cd, Cr, Cu and (iii) As, Cs, Rb, Sr, V.

References

[1] B.Wyrzykowska,K.Szymczyk, H.Ichichashi, J.Falandysz,B.Skwarzec and S. Yamasaki. *Journal of Agricultural and Food Chemistry*, 49 (2001) 3425-3431.

Application of dynamic headspace and GC-MS technique for the determination of oxygenated volatile organic compounds in industrial wastewater

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk and A. Fernandes

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland,

E-mail: grzegorz.boczkaj@gmail.com

P2-04

As a result of the industrial processes activities, a huge quantities of highly toxic wastewater are produced, which contains high concentrations of volatile organic compounds (VOCs). Among the wide range of VOCs, particular impact on environmental pollution have the oxygenated volatile organic compounds (O-VOCs). Because of their negative impact on health and the environment, it is necessary to identify individual compounds, and monitoring changes in concentrations O-VOCs in the effluents.

The work presents a procedure for the determination of oxygenated volatile organic compounds in postoxidative effluents from the production of petroleum asphalt using dynamic headspace coupled to gas chromatograph-mass spectrometry in the selected ion monitoring mode (DHS-GC-MS). Optimization of the method for the reference compounds (i.e. ketones, alcohols, aldehydes, esters, ethers, phenols) allowed to achieve a low detection limits, good reproducibility and a wide linear range for quantitative analysis. The analysis of raw wastewater samples revealed presence of mainly ketones, alcohols and aldehydes in concentrations ranging from 0.01 ppm to 118.61 ppm. Additionally, studies were performed using a SCAN mode, for the determination of other compounds from the group of O-VOCs. As a result, nine other compounds have been identified, for which the approximate concentration was determined in samples of raw effluents, and wastewater samples purified with chemical treatment.

This paper proves the need of O-VOCs groups monitoring in the chemical processes of purification of industrial wastewater, due to the presence of secondary pollutants. In the samples treated with various oxidation processes there was a significant increase in the content of cyclic and aliphatic alcohols, as well as phenol and substituted phenols.

Acknowledgements: The authors gratefully acknowledge the financial support from the National Science Center, Warsaw, Poland – decision no. DEC-2013/09/D/ST8/03973.

Studies of VOC degradation using Advanced Oxidation Processes (AOP) by means of "GREEN" extraction method and GC-MS technique

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk and A. Fernandes

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P2-05

Advanced Oxidation Processes (AOP) are an effective method to reduce the content of toxic pollutants in wastewater. In order to select the most appropriate method, which has the highest degree of reduction of volatile organic compounds (VOCs) in wastewater, a series of tests should be carried out. For this purpose first of all, summary parameters are determined such as chemical oxygen demand (COD) and biochemical oxygen demand (BOD), however, these parameters do not provide the complete information on the reduction of the individual compounds. In order to obtain a detailed data of the changes taking place during the oxidation of VOCs, more advanced analytical techniques are used, mainly the gas chromatography. This technique coupled with a suitably selected the detector and the sample preparation method, enables to monitor changes in the content of compounds, often present in very low concentrations in samples having a complex matrix.

The paper presents a novel analytical method allowing process control of changes in the content of VOCs using dispersive liquid - liquid microextraction and gas chromatography coupled to mass spectrometry (DLLME-GC-MS) in samples of industrial wastewater, treated with various chemical oxidation processes. The studies proved suitability of the method for the determination of analytes in a wide range of concentrations. The applied method also showed low values of the limit of detection and good repeatability.

It was also shown that when using some of the AOP methods, the increase in the content of some groups of the compounds takes place in comparison to their content in the raw wastewater. The reason for this phenomenon is the formation of secondary contamination compounds from the group of alcohols and phenols.

Acknowledgements: The authors gratefully acknowledge the financial support from the National Science Center, Warsaw, Poland – decision no. DEC-2013/09/D/ST8/03973.

Matrix solid-phase dispersion for the determination of antidepressants and antipsychotics in human hair by LC- Hybrid LTQ Orbitrap MS

E. Trantopoulos[1], V. Boti[1], V. Boumba[2] and T. Albanis[1]

[1] Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, Ioannina 45110, Greece
[2] Department of Forensic Medicine and Toxicology, Medical School, University of Ioannina, Ioannina 45110, Greece

E-mail: vboti@cc.uoi.gr

P2-06

In the present study a simple and sensitive method for the determination of seven antidepressants and antipsychotics (clozapine, olanzapine, haloperidol, mirtazapine, venlafaxine, amisulpride and carbamazepine) in human hair has been developed and validated. Human hair samples were collected from a healthy volunteer. Sample preparation was carried out using the matrix solid phase dispersion (MSPD) method. Hair sample (0.1 g) was digested in 1 mL of 1 M NaOH (80 °C, 20 min) and subsequently pH was readjusted to 9.0-10.0 with HCl. Then, the sample was mixed and dispersed using Alumina as the sorbent material and $MgSO_4$ as dehydrating agent. The blend was transferred to a polypropylene cartridge and analytes were eluted with methanol. The extract, was then evaporated under a gentle stream of nitrogen till 1 mL and further subjected to clean up by transferring the aliquot to centrifuge tube containing $MgSO_4$ and PSA. The tube was vigorously mixed for 1 min and centrifuged for 10 min to 4000 rpm. Finally, the supernatant was collected and after evaporated till dryness, the residue was reconstituted in 100 μL methanol and injected into the chromatographic system. Detection of the target analytes was performed using an LC- Hybrid LTQ –Orbitrap MS system in positive ionization mode in a total run of 10 min.
The validation scheme followed was based on the US Food and Drug Administration FDA [1]. Good linearity was obtained in all cases exhibiting excellent coefficients of determination (R^2). The method precision achieved in terms of repeatability and within-lab reproducibility, was low enough, expressed as relative standard deviation (R.S.D.), complying with the requirements of US FDA document (≤10%). Recoveries obtained were satisfactory for all analytes (above 70%) while limits of detection found at the low ppb level. The proposed method was validated with a view to be applied to the analysis of human hair of psychiatric patients of different treatment.

Acknowledgments: This study has been funded by the European Regional Development Fund-ERDF (MIS: 380379) through the Operational Program "THESSALY, MAINLAND GREECE AND EPIRUS 2007-2013" of the National Strategic Reference Framework (NSRF 2007-2013). The authors would also like to thank the Unit of Environmental, Organic and Biochemical high resolution analysis-ORBITRAP-LC-MS of the University of Ioannina for providing access to the facilities.

References

[1] FDA Guidance for Industry on Biomedical Method Validation, 2001, http://www.fda.gov/Drugs/default.htm

In-tube roasting combined with GC-MS profiling as new approach to evaluate the aroma potential of Tanzanian cocoa beans

A. De Winne[1] and J. Van Durme[1]

[1]KULeuven Research Unit Molecular Odour Chemistry - Technology Campus Ghent, Gebroeders De Smetstraat 1, 9000 Gent, Belgium

E-mail: Ann. De Winne@biw.kuleuven.be

P2-07

The aroma of cocoa has already been extensively studied. The flavour quality of chocolate usually depends on the cocoa bean origin and fermentation conditions, each resulting in specific and distinct flavour characteristics [1]. The final flavour formation is particularly formed during the roasting process, due to the chemical transformations that take place during this thermal processing step. In this work research attention is given to an innovative application of a Thermal Desorption Unit (TDU) to form roasting compounds during the sample preparation step immediately followed by a hyphenated GC-MS-(ODP) method.

Thermal desorption has some key advantages over other sample preparation methods. The requirement for only a small amount of sample amount and reduced time for analysis made is suitable for especially qualitative and quantitative component analysis.

In this study, the effect of different in-tube roasting temperatures (110°C, 150°C, 200°C) and different roasting times (5 min, 20 min, 40 min) was measured on both fermented and low fermented Tanzanian cocoa beans. The formation of different typical cocoa roasting aroma compounds (aldehydes, ketones, acids, esters) was measured; special attention was given to formation of pyrazines.

It can be concluded that this innovative on-line analytical method has the potential to replace labor-intensive aroma precursor measurements (e.g. amino acids, sugars, etc.) to objectively assess the aroma potential of cocoa beans and hence evaluate their overall quality.

References

[1] A. De Winne, P. D. Tran, D. Van De Walle, K. Dewettinck and J. Van Durme, *Novel Approaches in Food Industry* (Turkey, May 2014).

Development and validation of a novel LC-MS/MS method for the quantitative determination of brinzolamide in dried blood spots

A. Foivas[1], Y. Dotsikas[1], A. Malenović[2], N. Kostić[2], M. Božić[3,4], M. Knežević[3,4] and Y.L. Loukas[1]

[1]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Athens, PanepistimioupoliZografou GR - 157 71, Athens, Greece
[2]Department of Drug Analysis, Faculty of Pharmacy, University of Belgrade, Vojvode Stepe 450, Belgrade, Serbia
[3]Faculty of Medicine, University of Belgrade, Belgrade, Serbia
[4]Adnexal department, Clinic of Eye Diseases Clinical Center of Serbia, Belgrade, Serbia

E-mail: idotsik@pharm.uoa.gr

P2-08

Over the last decade, dried blood spots(DBS)sampling technique has emerged as a promising substitute of traditional liquid bio-matrices[1]. The most prominent advantages are the low blood volume requirement, the transportation and storage without special treatment and the enhanced analytes stability.
Brinzolamideis a carbonic anhydrase II inhibitor indicated for the treatment of elevated intraocular pressure in patients with ocular hypertension or open-angle glaucoma. Following topical ocular administration, usually as ophthalmic suspension, brinzolamide is absorbed into the systematic circulation exhibiting an 111-day half time in blood. In blood, brinzolamide distributes almost exclusively into red blood cells, rendering its determination in plasma very difficult [2]. To this purpose, DBS may serve as the ideal material for analytes with similar 'behavior'.
In the current study, arapid and sensitive method based on LC-ESI-QTOF-MS/MS was developed for the determination of brinzolamide in DBS. An isocratic mobile phase consisting of methanol and 10mM ammonium formate (90:10 v/v) was utilized in conjunction with a Cyano analytical column. The flow rate was adjusted at 0.350 mL/min yielding retention times of 1.7 and 1.9min for brinzolamide and internal standardrabeprazole, respectively. The calibration curve was linear over the range 0.500 - 20.0 μg/mL providing r^2>0.99. The validation of the proposed method was performed in compliance with the EMA and FDA guidelines assessing all major performance characteristics.Inter- and intra- assay precisions were less than 16.3%, while inter- and intra- assay accuracies varied from 87.6 to 117%. No matrix effect was observed and the mean analyte recovery was 93.6%.
The method was successfully applied toreal DBS samples from patientsin steady state receiving brinzolamide ophthalmic suspension 1%. Initial concentrations were corrected due to hematocrit effect, using image processing algorithm written in Matlab.

References

[1] M.Wagner, D.Tonoli, E.Varesio and G.Hopfgartner, *Mass Spectrom. Rev*, 9999 (2014) 1-78
[2] R.Kadam, G.Jadhav, M.Ogidigben and U.Kompella, *Drug Metab. Dispos.* 39 (2011) 1529–1537

Inductively Coupled Plasma-Mass Spectrometric analysis as a tool for Rare Earth Elements analysis: A case study on mineral processing of REE ores

V. Angelatou, N. Xirokostas, C.-A. Drosou, E.I.P. Drosos and D. Eliopoulos

Institute of Geology & Mineral Exploration (IGME)
NATIONAL CENTER OF SUSTAINABLE DEVELOPMENT
1st Spyros Louis str., Olympic Village - Entrance C
13677 Acharnes – Athens - Greece

E-mail: vasaggelatou@igme.gr

ICP-MS is a very powerful tool when it comes to the determination of trace elements in earth sciences. The aim of this paper is to provide an overview of the use of ICP-MS in the determination of rare earth elements on samples produced from mineral processing of REE ores in the frame of an ongoing European Project (EURARE). The feed material (monazite – xenotime ores) was beneficiated by applying physical, low cost and environmental friendly methods, taking in advantage of the different properties of the minerals (magnetic susceptibility, specific gravity, grain size liberation).

Data are presented for 17 analytes in four international standard reference materials (Geostandards, Geological Survey of Canada) and in samples obtained from Kavala N. Greece region. The sample preparation as a first step includes a dissolution with aqua regia and HF (in order to solve dissolution problems in siliceous samples) in Teflon® containers and then the residue was chemically attacked with HCl and H_2O_2. The samples were preserved in 5% concentrated HCl. The instrumental sensitivity of ICP-MS was measured by external calibration solutions with matrix correction.

The accuracy of the measurements was verified by mass balance calculations.

References

[1] G.A. Jenner, H.P.Longerich, S.E. Jackson and B.J. Fryer, *Chemical Geology*, 83 (1990) 133-148
[2] A.R. Date and A.L. Gray, Spectrochimica Acta, 40B (1985) 115-122
[3] H.P.Longerich, G.A. Jenner, B.J. Fryer and S.E. Jackson, *Chemical Geology*, 83 (1990) 105-118

Qualitative analysis of compounds in commercial fragrance mixture of essential oils (Rose Josephine) for preparation of the perfume using gas chromatography-mass spectrometry

S. Surmová, A. Eisner, M. Adam, P. Bajerová, T. Bajer and K. Ventura

University of Pardubice, Faculty of Chemical Technology, Department of Analytical Chemistry, Studentska 573, 532 10 Pardubice, Czech Republic

E-mail: ales.eisner@upce.cz

P2-10

Perfume is a general designation for a mixture of essential oils. Each perfume is composed of a wide range of volatile aromatic compounds. Each compound has its characteristic odor and together they make the characteristic aroma of the perfume. Odors play a crucial role in human behavior. A pleasant smell can have a calming effect on humans whereas unpleasant smells can change our mood negatively. The use of different smells can cause a variety of feelings and desires and it may emphasize the personality of the wearer.

The commercial fragrance mixture of essential oils, usually for preparation of the perfume, was purchased from a perfumery and was studied by GC-FID and GC-MS. Ninety-two peaks were detected and fifty-seven of them were identified: fourteen hydrocarbons, thirteen alcohols, twelve esters, seven ketones, five phenols, three aldehydes and one acetal, (ep)oxide and lactone. A significant group were esters, especially ethylene brassylate (29.98 %), methyl-dihydrojasmonate (cis- and trans-form 24.57 %), and isopropyl myristate (3.03 %). Other important compounds were cedryl methyl ketone (6.21 %), pentadecanolide (5.55 %), citronellol (4.66 %), phenylethyl alcohol (4.53 %), and β-ionone (4.17 %).

Highly efficient sample preparation and quantification of N-nitroso compounds in water samples using solid-phase extraction and ultra-performance liquid chromatography-tandem mass spectrometry

Y. Kadmi[1,2], L. Favier[1,2], A. I. Simion[3] and D. Wolbert[1,2]

[1]Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR 6226, 11 Allée de Beaulieu, CS 50837, 35708 Rennes Cedex 7, France
[2]Université Européenne de Bretagne, France
[3]"Vasile Alecsandri" University of Bacau, Faculty of Engineering, Department of Chemical and Food Engineering,157 Calea Marasesti, 600115 Bacau, Romania

E-mail: yassine.kadmi@gmail.com ; lidia.favier@ensc-rennes.fr

Water disinfection is a widely used and efficient process to reduce the occurrence of water-borne diseases, and has been one of the most successful public health advances of the last century. However, in addition to microorganism inactivation, chemical disinfectants such as chlorine also react with natural organic matter and bromide ion present in water to form numerous disinfection by-products (DBPs). Among them, trihalomethanes and haloacetic acids, represent a major class of DBPs currently regulated in drinking water [1]. N-nitrosamines, as a group of emerging DBPs, have recently caused significant concerns because, these pollutants are considered generally much more carcinogens than the currently regulated ones. Thus, the determination of ultra-trace levels of these compounds in water samples is urgently needed. In this study, a fast, highly sensitive and simple solid-phase extraction method (SPE) combined with ultra-performance liquid chromatography coupled with tandem mass spectrometry (UPLC/MS/MS) was developed for the analysis of ultra-trace levels of N-nitrosamines in water samples. Chromatographic separation was performed using an Acquity UPLC C18 column and a mobile phase consisting of acetonitrile, water, and formic acid (60:40:0.1, v/v/v) at a flow rate of 0.4 mL/min. The run time of the method was three minutes. The performance of the proposed method was studied in terms of linear calibration curves, linearity ($r^2 \geq 0.997$), precision (<4.8%), accuracy (between 99% and 105%), low limits of quantification (0.08–0.32 ng/L). The extraction recoveries of the analytes were within the range of 96–101% and the relative standard deviations were less than 5%. The matrix effect was within 93–104% at all quality control levels. In conclusion, the results showed that the developed method is simple, highly sensitive and accurate for the simultaneous determination of N-nitrosamines at ultra-traces levels (ng/L) in different types of water samples. Therefore, the excellent performance of the developed method, as well as the short analysis time makes it a promising analytical tool for the screening of N-nitrosamines in water samples.

References

[1] L. Meng, S. Wu, F. Ma, A. Jia and J. Hu, *Journal of Chromatography A*, 1217 (2010) 4873-4876.

Improving the quality characteristics of marc spirits produced by adding dried figs

P. Giannouzi, P. G. Demertzis and K. Akrida-Demertzi

Laboratory of Food Chemistry, Department of Chemistry, University of Ioannina, P.O. Box 1186, GR–45110 Ioannina, Greece

*E-mail: kakrida@uoi.gr

P2-12

The quality of alcoholic beverage «tsipouro» is a result of several factors. To produce a quality distillate the raw material is of special importance. The variability in aroma depends on soil-climatic conditions, cultivar, maturity, raw material hygienic status, processing and storage conditions. Moreover, the organoleptic quality of a distillate is significantly related to the applied distillation technology which includes the type of distillation apparatus, the methodology, the separation of the three distillation fractions (head, heart, and tail) as well as the conditions and time of distillation.

In the present study, several marc spirit (tsipouro) samples prepared with and without the addition of dried figs were analyzed. Marcs for the investigated distillates came from Vitis vinifera var. Debina grape cultivar (Epirus, north-western Greece). Dried figs were supplied by Sykiki- Kalamata. Tsipouro spirits were produced by distillation of raw material without adding any aromatic plants or herbs, therefore its aroma is attributed to the grape cultivars used volatile alcoholic fermentation by-products and/or to products of chemical reactions between the above mentioned compounds, as well as the addition of dried figs. The main objectives of the present study were: i) the identification and semi-quantification of the principal volatile substances and ii) the organoleptic quality of distillates. The separation and identification of the volatile compounds was performed by HS-SPME combined with GC/MS analysis. For the semi-quantification of the identified volatile compounds, 2-octanol was used as internal standard. A total number of 31 compounds belonging to the chemical categories of alcohols, phenols, aldehydes, ethers and terpenes were identified. In spirits prepared by adding dried figs, a number of volatile compounds characteristic of the aromatic profile of the distillate were identified in higher concentrations. Moreover, additional substances whose presence is due to the addition of dried figs were identified.

The sensory examination of the studied distillates showed that the spirits with the addition of dried figs were more acceptable.

Development of a sample preparation method for manganese speciation in plant

E. Grygo-Szymanko, A. Tobiasz, A. Wisłocka, D. Dudek-Adamska, N. Miliszkiewicz and S. Walas

Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena St. 3, 30-060 Krakow, Poland

E-mail: tobiasz@chemia.uj.edu.pl

Manganese is known to be an essential micronutrient for proper functioning of plants via activation of a several enzymes involved in photosynthesis, respiration and the synthesis of proteins, acyl lipids and carbohydrates in plants organisms [1]. Absorption of manganese by plant depends on the ability of the plant to transfer the metal ions across the soil–root barrier as protein complexes (e.g. AtIRT1, Nramp) or non-protein amino acids (e.g. nicotianamine, glutathione, Asn, Gln, Ser) [2].
Since manganese can be one of the factors responsible for stress reaction and its bioavailability and toxicity to plants strongly relates to different forms, it is important to be able to determine each species separately.
In speciation analysis, extraction of the species plays crucial role especially due to the problems with the stability of complexes mainly related to the matrix of samples and chosen technique of analysis. The main aim of this work was to develop plant samples preparation approach (e.g Triticum L.) for prospective determination of manganese species by chromatographic technique coupled to ICP-MS. Several extraction procedures for the isolation of water and protein Mn-fractions, were tested. The process of extraction (including shaking, heating and sonication) was optimized. The comparison of centrifugation and filtration processes to separate extracts from solid phase was done. To assess the efficiency of extraction total manganese in plant samples was also determined by ICP-MS, after microwave-assisted digestion of fresh, dry, freeze-dry and freeze samples. The quality of the total procedure was controlled analyzing reference material of wheat (IPW 682) and oriental tobacco leaves (CTA-OTL-1). Simultaneously, the impact of storage in different conditions (refrigerator, freezer and room temperature) on extracts was investigated.

Acknowledgments: The research was financed by the National Science Center, Poland, project no. 2013/11/D/ST4/02839.

References

[1] M. Boojar and F. Goodarzi, *Ecotoxicology and Environmental Safety*, 71 (2008) 692–699
[2] J. K. Pittman, *The New Phytologist*, 167 (2005) 733–742

Early identification of etiological agents of fungal infection and assessment of susceptibility antifungal drug, amphotericin B, by advanced separation techniques in human blood

M. Horká[1], K. Šlais[1], J. Šalplachta[1], F. Růžička[2], M. Tesařová[1], P. Karásek[1] and M. Roth[1]

[1] Institute of the Analytical Chemistry Academy of Sciences of the Czech Republic, v. v. i., Veveří 97, 602 00 Brno, Czech Republic -1

[2]The Department of Microbiology, Faculty of Medicine, Masaryk University and St. Anne's University Hospital, Brno, Pekařská 53, 65691 Brno, Czech Republic -2

E-mail: horka@iach.cz

P2-14

Fungal healthcare-associated infections are characterized by difficult therapy and high mortality. Early identification of an etiological agent of these infections, selection and monitoring of the effectiveness of an appropriate antifungal therapy are essential for a successful treatment outcome. The most common fungi causing these infections are yeasts of the genus *Candida*. From the antifungal drugs polyenes exhibit the broadest range of activity. However, only amphotericin B (AMB) remain in widespread clinical use [1] with a relatively few examples of mycological resistance to this drug. The major issue is in AMB toxicity and adverse side effects such as nephrotoxicity, renal failure etc. [2]. Minimum inhibitory concentrations range from 0.03 to 1 □g mL^{-1} (i.e. from 3.25 to 108 × 10^{-8} mol L^{-1}) was determined for a variety of organisms including strains of, e.g., Candida, Asperigillus [3]. HPLC is the universal rapid, sensitive technique widely applied for this purposes [4]. The detection limits were found as 250 ng mL^{-1} in water and approximmately as 280 ng mL^{-1} in spiked normal organs [5]. AMB was also separated using MEKC with diode array UV detection at 407 nm [6]. The detection limit was 1 □g mL^{-1}.

We tested pre-concentration of fungal pathogens, and AMB (0.3 ng mL^{-1}) from blood on segmented strip, and their subsequent CZE, CIEF (UV detection) as fast and low-cost methods to detect these analytes in FS capillaries etched with supercritical water and modified with (3-glycidyloxypropyl)trimethoxysilane. Simultaneously, the differences in the chemotaxonomy fingerprints of the microorganisms can be utilized by MALDI-TOF MS.

Acknowledgements: This work was supported by the Ministry of the Interior of the Czech Republic (Grant VG20102015023 and VG20112015021), and by the Academy of Sciences of the Czech Republic (Institutional Support RVO:68081715).

References

[1] P. Chandrasekar and J. Antimicrob. *Chemoth*., 66 (2011) 457-465.
[2] D. Ellis and J. Antimicrob. *Chemoth*., 49 (2002) 7-10.
[3] R.M.C. Dawson, D.C. Elliot, W.H, Elliott and K.M.Jones, Data for Biochemical Research (3rd ed.) Oxford University Press, NY, USA, 1989; 296-297.
[4] R. Cantón, M. Akóva and Y. Carmeli, *et al. Clin. Microbiol. Infect.*, 18 (2012) 413-431.
[5] A.P. Magiorakos, A. Srinivasan and R.B. Carey *et al. Clin. Microbiol. Infect*, 18 (2012) 268-281.
[6] K. Makino, M. Hirakawa, Y. Goto, K. Nakashima, Y. Kataoka and R. Oishi, *Electrophoresis*, 19 (1998) 2930-2934.

Determination of multiclass pesticides in water samples combining Solid Phase Extraction (SPE) coupled to GC-MS and LC-MS. A case study: Louros River (N.W. Greece)

M. Kapsi, Ch. Tsoutsi and T. Albanis

Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, Panepistimioupolis, Ioannina, 45110, Greece

e-mail: talbanis@cc.uoi.gr

P2-15

Worldwide pesticide usage has increased dramatically during the last two decades. Pesticides are the most dangerous environmental pollutants because of their stability, mobility, and long-term effects on living organisms [1]. Therefore their determination is of a great importance.

The aim of this work, was to develop an efficient method on the basis of solid phase extraction (SPE) technique followed by gas chromatography and liquid chromatography coupled mass spectrometric analysis for the determination of thirty four multiclass pesticides in natural waters [2].

The proposed methodology showed good linear response with R^2 values in the range of 0.990-0.999. Values of relative recoveries located within the acceptable range of (67.32-104.99%). Limits of detection (LODs) were estimated on the basis of 3:1 signal-to noise ratios obtained with standards containing the compounds of interest at low concentration level, ranged from (7-30ng/L). The repeatability and reproducibility of measurements, expressed as relative standard deviation (RSD), was less than 10% for analytes.

The method was applied in a case-control study carried out on a Louros river for a period of one year. An amount of 35 representative water samples (river, lake and sea water samples) were collected in the whole sampling period. The ecological risk associate with pesticide contamination was assessed to estimate the preliminary risk posed to studied ecosystem. The most frequently detected pesticides were: Iprodione, Pendimethaline, Fenpyroximate, Triadimenol, Quizalofop- ethyl, Tebufenpyrad, Endosulfan-alpha, Endosulfan-beta, Endosulfan-sulfate and Myclobutanil. Concentrations of individual compounds ranged from below limit of quantification to 0.451μg/L. The performance results confirm the usefulness of the proposed methodology for the analysis of multiclass pesticides in natural waters.

Acknowledgments: This research project has been co-financed by the European Union (European Regional Development Fund- ERDF) and Greek national funds through the Operational Program "THESSALY- MAINLAND GREECE AND EPIRUS-2007-2013" of the National Strategic Reference Framework (NSRF 2007-2013).

References

[1] I. Konstantinou, D. Hela and T. Albanis *Environmental Pollution,* 141 (2006) 555-570.

[2] M.Kapsi, C.Tsoutsi and T. Albanis (18-21September 2014). 8th European Conference on Pesticides and Related Organic Micro-Pollutants in the Environment, Ioannina-Greece.

Determination of various pesticides in fresh waters by means of high resolution & high mass accuracy hybrid linear ion- trap- orbitrap mass spectrometry

Ch. Nannou[1], V. Boti[1], M. Tsomi[1], G. Patakioutas[1], T. Albanis[1] and G. Karras[2]

[1]Dept. of Chemistry, University of Ioannina, 45 110, Ioannina, GREECE
[2]Dept. of Agricultural Technology, TEI of Epirus, 47100, Kostakioi, Arta, GREECE

E-mail: chnannou@cc.uoi.gr

P2-16

The extended use of pesticides for agricultural and non-agricultural purposes has led to their occurence in various environmental matrices. Pesticide residues enter fresh waters mainly through agricultural run-off. Both parent pesticides and metabolites may cause a toxic action in organisms of freshwater systems, whenever the concentration of a compound is sufficient to trigger such effect. The analysis of pesticide residues in a variety of environmental matrices contributes to ensure their safety and quality. Until recently, multi-residue analysis of such compounds at trace levels has been mainly carried out by means of GC and LC coupled to mass spectrometry. Currently, scientific interest has also been shifted to even more accurate and sensitive detectors. In that direction, the use of high-resolution mass spectrometers (LC-HRMS) and especially Orbitrap technologies enables the acquisition of a theoretically unlimited number of species by means of accurate mass measurements in full-scan mode. This allows obtaining the elemental composition of acquired ions, useful for identification of targeted and untargeted compounds, metabolites, or transformation products [1].
In the present study, an SPE procedure was evaluated in order to be applied for the estimation of the pollutant load and its seasonal distribution in natural waters of the Prefecture of Epirus (Aracthos and Louros rivers, Amvrakikos gulf), N.W. Greece. Hybrid LTQ Orbitrap mass spectrometry was employed for the ultra-trace detection and quantification of target pesticides and finally was successfully applied to the analysis of waters. The identification of the positive findings is accomplished with the data from accurate masses of the target ions, based on the full-scan exact mass measurement of [M+H]+ ions, along with retention time data and characteristic on-source fragment ions. The results obtained confirm that high-resolution mass spectrometry is a helpful and reliable tool for the identification and quantitation of pesticide residues, providing at the same time high accuracy.

Acknowledgments: The research is implemented through the Operational Program "Education and Lifelong Learning" and is co-financed by the European Union (European Social Fund) and Greek national funds.
The authors would like to thank the Unit of Environmental, Organic and Biochemical high resolution analysis-ORBITRAP-LC-MS of the University of Ioannina for providing access to the facilities.

References

[1] J. Robles-Molina, F.J. Lara-Ortega, B. Gilbert-López, J.F. García-Reyes, A. Molina-Díaz, *J. Chromatogr. A* (2014) 1350, 30-43.

Effect of the addition of berries in the antioxidant capacity of traditional Greek spirits

A.K. Kosma, P.G. Demertzis and K. Akrida-Demertzi

Laboratory of Food Chemistry, Department of Chemistry, University of Ioannina, P.O. Box 1186, GR–45110 Ioannina, Greece

E-mail: kakrida@uoi.gr

P2-17

In Epirus- Greece significant quantities of distillates from arbutus (koumaro) without addition of chemicals are produced. The distillates have an antioxidant capacity which can be enhanced by adding a certain amount of fresh berries. This addition will also improve the aesthetic appearance of the product.

In this study several samples of Greek arbutus distillates from different producers in the area of Epirus with addition of ten organic fruits that have strong antioxidant capacity (strawberries, wild strawberries, raspberries, black and white mulberries, red and black gooseberries, elderflower, cranberries and blackberries) at concentrations of 5, 10 and 15%, were studied. Berries were added immediately after distillation and the samples were stored for 12 months at room temperature. At specific time intervals (0, 3, 6, 9, and 12 months) determinations of total phenols by the Folin-Ciocalteu method and the antioxidant capacity by DPPH method were performed.

In all samples, an increase of antioxidant capacity and amount of total phenols with time and concentration of berries added was generally observed, in comparison with the original distillates. Of the samples studied, the largest increase in antioxidant capacity and total phenols content was found in distillates containing cranberries and raspberries.

In conclusion, it can be said that adding berries to spirits can lead to beneficial health properties.

MALDI-TOF MS in identification and discrimination of *Staphylococcus aureus* strains

J. Šalplachta[1], F. Růžička[2] and M. Horká[1]

[1]Institute of Analytical Chemistry of the ASCR, v. v. i., Veveří 97, 60200 Brno, Czech Republic
[2]Department of Microbiology, Faculty of Medicine, Masaryk University and St. Anne's University Hospital, Brno, Pekařská 53, 65691 Brno, Czech Republic

E-mail: salplachta@iach.cz

P2-18

Staphylococcus aureus is facultative anaerobic Gram-positive spherical bacteria and an important human pathogen frequently resistant to a wide range of antibiotics. Although *S. aureus* can commonly occur on skin, in the nose, and less commonly in the throat, it is responsible for wide range of infections. The illnesses caused by *S. aureus* can vary from minor skin infections to life-threatening diseases such as pneumonia, endocarditis, meningitis, and sepsis. *Staphylococcus aureus* is the major cause of nosocomial infections and it has an exceptional capacity to acquire resistance to many commonly used antibiotics. Moreover, the number of resistant strains has rapidly increased in recent years. In particular, methicillin-resistant *S. aureus* (MRSA) strains represent a serious problem worldwide. Rapid and accurate method for discrimination between MRSA and methicillin-sensitive *S. aureus* (MSSA) strains is essential for appropriate and timely treatment of the infection.

Potential of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) to differentiate MRSA and MSSA strains was investigated in the present study. In this respect, different sample preparation strategies were used. Three types of bacterial samples were prepared, intact cells, cell lysates, and "washed pellets" (the residue after lysis). In addition, the examined bacteria were cultivated with certain amount of various antibiotics. Some of the obtained results are very promising and the suitability of different approaches for the differentiation MRSA and MSSA strains using MALDI-TOF MS will be discussed.

Acknowledgements: This work was supported by the grants of Ministry of Interior No. VG20102015023 and No. VG20112015021 and by the institutional support RVO: 68081715.

Analysis of glycoconjugates from primary brain tumors using a complex mass spectrometric methodology

A.F. Serb[1], L. Bozin[1], A. Dema[1], M. Georgescu[1], E. Sisu[1] and A.D. Zamfir[2, 3]

[1]"Victor Babes" University of Medicine and Pharmacy, Timisoara, Romania; [2]"Aurel Vlaicu" University of Arad, Romania, [3] Mass Spectrometry Laboratory, National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania

E-mail: aserb@umft.ro

P2-19

Carbohydrates are found on the outer surface of all eukaryotic cell membranes, attached to the membrane proteins and/or sometimes to the lipids forming glycoconjugates. They create a cell coat or glycocalyx outside the cell membrane, which is involved in protection and cell-cell recognition and interaction. Glycosphingolipids constitute a highly important class of glycoconjugates – bioactive molecules which are made up of lipids and an attached carbohydrate. Gangliosides - acidic glycosphingolipids - are extremely rich in glial cells and neurons, making them a promising lead for various brain disorders biomarkers, especially tumors since these molecules have been demonstrated to accelerate the formation and progression of tumors [1, 2]. Although an increasing interest in aberrant glycosylation associated with cancer exists, true research progression and a comprehensive investigation of cancer-specific glycans can only be achieved with success with the aid of combined novel high-throughput "omic" approaches. Therefore, the present study tackles a comparative investigation of the glycosphingolipid profile from glioblastoma *vs.* healthy human brain using a complex methodology made up of multiple steps of samples extraction/purification aimed at obtaining the native acidic mixtures of glycosphingolipids, followed by HPTLC separation of the main species of glycosphingolipid, fotodensitometric analysis, fully-automated chip-based mass spectrometric (MS) screening of the purified mixtures and structural characterization of isolated glycoforms through tandem mass spectrometry (MS/MS). The data obtained demonstrated a highly altered profile of gangliosides in glioblastoma *vs.* healthy tissue, with an increased proportion of short ganglioside species, which contain a disaccharide group attached to the ceramide, from mono (GM3) - to pentasyalilated (GP3) and of asialo glycoforms (mostly GA1 type), all of which demonstrate the necessity for consideration and for additional studies of these molecules as being linked to the development of tumors, studies in all the areas of oncology and the field of neurooncology in particular.

Acknowledgements: This work was supported by the Romanian National Authority for Scientific Research (CNCS-UEFISCDI) through projects PD 43/2011 and PN-II-PCCA-2011-142

References

[1] S. Hakomori and K. Handa, *FEBS Lett.* , 531 (2002) 88-92 .
[2] E.J. Joo, A. Weyers, G.Li , L. Gasimli , L. Li , W.J. Choi , K.B. Lee and R.J. Linhardt, *OMICS.*, 18 (2014), 231-241.

Correlations between arsenolipids, organic and inorganic forms of arsenic, mercury and selenium in muscles and cephalothoraxes of *Aristaeomorpha foliacea* shrimp.

G. Soultani[1, 3], V. Sele[2], R.R. Rasmussen[3], I. Pasias[1], E. Stathopoulou[1], N. Thomaidis[1], M. Scoullos[1] and J. J. Sloth[2, 3]

[1]National and Kapodistrian University of Athens (NKUA), Panepistimioupolis Zographou, 15771 Athens, Greece
[2]National Institute of Nutrition and Seafood Research (NIFES), N-5817 Bergen, Norway
[3]National Food Institute, Technical University of Denmark, Mørkhøj Bygade 19, DK 2860 Søborg, Denmark

E-mail: gesoultan@chem.uoa.gr

P2-20

A Mediterranean shrimp from the deep waters of the Ionian Sea was studied in terms of its content of organic and inorganic As, Hg and Se in muscles and cephalothoraxes. Total As concentration ranges from 1 to 100 mg/kg w.w in marine organisms and it is found as inorganic (the most toxic form, typically found in low concentrations) and as organic (considered as less- or non-toxic, and typically found in high levels). Arsenolipids, a group of lipophilic of arsenic-containing compounds, has been reported in concentrations from 1 to 50 mg/kg in marine oils [1]. Hg, a toxic element, is typically determined in low levels in crustaceans. Se is believed to have an antagonistic protective effect against the toxicity of Hg and hence the ratio of these two elements is interesting to be studied in marine organisms. The aim of the present study was to determine the levels of these metals in order to evaluate the food safety of this shrimp.

ICP-MS, HPLC-ICPMS and CVAFS were used for the analysis. Total As in muscles was 16.3 mg/kg w.w., while in cephalothoraxes much higher concentrations (32.7 mg/kg w.w.) were observed. The inorganic form of As in the shrimp was detected only in cephalothoraxes at low levels (0.9 iAs μg/kg w.w.) and not at all in the edible muscle tissue. Arsenolipids comprised only 0.4% of the total organic As in the muscles and 1.9% of the organic As in cephalothoraxes. Analysis of the cephalothorax extract showed the existence of several arsenolipids in this type of shrimp. The rest of the organic As, including the water-soluble compounds, mainly arsenobetaine, which typically is the predominant arsenic compound in marine organisms, was calculated. As far as Hg is concerned according to the European Legislation for heavy metals in foods, it has a maximum level of 0.5 mg/Kg w.w. in seafood. The studied samples had lower concentration than the maximum level. The concentration of Se in the whole shrimp (sum of both tissues) was 3 times higher than Hg concentration. Remarkably, Se content in cephalothoraxes was one folder higher. The correlation coefficient between these two metals had the highest value (-1.00). In conclusion, even though the levels of As were quite high, the largest proportion of total As was in organic form (primarily non-toxic) and the levels of Hg was lower than the permissible maximum level.

References

[1] V. Sele, J.J. Sloth, B. Holmelid, S. Valdersnes, K. Skov and H. Amlund, *Talanta*, 121 (2014) 89–96.

Determination of fatty acids and trace elements in muscles and cephalothoraxes of a Mediterranean red shrimp

G. Soultani[1,3], E. Stathopoulou[1], M. Kostakis[1], N. Thomaidis[1], M. Scoullos[1], C. Jacobsen[2] and J.J. Sloth[3]

[1]National and Kapodistrian University of Athens (NKUA), Panepistimioupolis Zographou, 15771 Athens, Greece
[2]National Food Institute, Technical University of Denmark, Building 221, DK-2800 Kgs. Lyngby, Denmark
[3]National Food Institute, Technical University of Denmark, Mørkhøj Bygade 19, DK- 2860 Søborg, Denmark

E-mail: gesoultan@chem.uoa.gr

Aristaeomorpha foliacea, shrimp from deep water of Ionian Sea, was studied in terms of its nutritional quality. Fatty acids of total (TL), neutral (NL) and polar (PL) lipids and the concentration of Mg, Mn, Fe, Ni, Cu, Zn and Cr were determined in muscles and cephalothoraxes. Cephalothoraxes were studied due to their economical value for the pharmaceutical industry in production of medicines and food supplements. Muscles were studied in order to observe whether this type of shrimp is suitable for human consumption.

The fat content of these tissues was determined by Bligh-Dyer extraction [1]. Solid Phase Extraction (SPE) was used to separate the total lipid to neutral and polar lipids. The fatty acids of these lipids were determined by Gas Chromatography (GC-FID). C16:0 and C18:0 were the most abundant saturated fatty acids in both tissues in TL, NL and PL. Cephalothoraxes were rich in monounsaturated fatty acids (MUFA) ranging from 35.5-51.1% mainly consisted by C18:1 ω-9, C18:1 ω-7, C16:1 ω-7 and C20:1 ω-11. The levels of MUFA in the muscles were lower than in the cephalothoraxes with the exception of the class of NL. Moreover, both muscles and cephalothoraxes were high in polyunsaturated fatty acids (PUFA) with a range of 23.6-43.7%. C22:6 ω-3 (DHA) and C20:5 ω-3 (EPA) were the dominant PUFA. The ratio ω:3/ω:6 was in agreement with the recommendations of the U.K. Department of Health. The levels of atherogenic (AI) and the thrombogenic (TI) indices were found really low.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis was used to measure the elements. Cephalothoraxes contained much higher concentrations in contrast to muscles. According to the guidelines of the US Nutrients Institute of Medicine and the Food and Nutrition Board [2], the estimated intake per meal size (EIm) was calculated for the edible tissue in order to assess the agreement with the Recommended Dietary Intake of the Greek law.

References

[1] E.G Bligh, and W.J. Dyer, *Canadian Journal of Biochemistry and Physiology*, 37 (1959) 911-917.
[2] Nutrients Institute of Medicine (US) Food and Nutrition Board. Washington (DC): Dietary Reference Intakes: A Risk Assessment Model for Establishing Upper Intake Levels for National, Academies Press (US); 1998

Preparation and evaluation of matrix-matched standards towards analysis of distribution of elements in historical bones by laser ablation inductively coupled plasma mass spectrometry

S. Walas, N. Miliszkiewicz, A. Tobiasz and E. Grygo-Szymanko

Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Ingardena St. 3, 30-060 Krakow, Poland

E-mail: walas@chemia.uj.edu.pl

P2-22

Atomic mass spectrometry with ionization by inductively coupled plasma and laser ablation sampling (LA-ICP MS) is widely applied for direct analyses of solid materials, yet in order to obtain accurate results it requires a complex calibration approach [1]. Application of this technique towards analysis of distribution of selected elements in bones is a challenging task mainly due to strong morphological diversification, incident to bones diagenesis. However better understanding of ablation process and interpretative possibilities in the area of anthropological studies are the main reasons weighted in favour of taking a try to determine concentration of selected elements in this material.

The main objective of the studies was to establish a versatile calibration approach for strontium determination in bones by LA-ICP MS. Calibration was based on solid standards in a form of pellets, matched to the matrix of bone samples by use of real bone material ground and mixed with a reference material of strontium carbonate (SRM 987). The time of milling and mixing was optimized to provide homogeneity of standard pellets, as well as pressure of pressing. The quality of prepared standards was checked by parallel studies carried out with ICP MS whereby portions of standards digested in nitric acid with a support of microwave radiation were analysed. Analytical signals obtained by analysis of solid samples with laser ablation were mathematically corrected with regard to the interferential influence of ^{87}Rb on ^{87}Sr. The stability of signals which is correlated with homogeneity of material was assessed with %RSD (relative standard error) values. Good correlation between determined and assumed values of total concentration of Sr in standard pellets was obtained, which proves correctness of preparation procedure. Those standards were successfully used for calibration of analysis of historical solid bone fragments by LA-ICP MS. It was observed that signals from strontium isotopes are affected by some other interferential effects which further assessment have to be undertaken. The next step of the studies will be to propose a method of signals standardization which leads to improvement of precision and repeatability of obtained analytical data.

Acknowledgements: The research concerning the reference method was carried out with the equipment purchased, thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.0100-12-023/08).

References

[1] N. Miliszkiewicz, S. Walas and A. Tobiasz, *J. Anal. At. Spectrom*., 30 (2015) 327-338.

UHPLC-MS/MS quantitative profiling of tryptophan related neuroactive substances in human serum and cerebrospinal fluid

E. Hényková[1], H. Přikrylová Vránová[3], P. Amakorová[1], T. Pospíšil[2], A. Zukauskaite[2], M. Vlčková[1], L. Urbánek[1], O. Novák[1], P. Kaňovský[3] and M. Strnad[1]

[1]Laboratory of Growth Regulators, Centre of the Region Haná for Biotechnological and Agricultural Research & Faculty of Sciences, Palacký University & Institute of Experimental Botany AS CR, v. v. i., Šlechtitelů 11, 783 71 Olomouc, Czech Republic
[2]Department of Chemical Biology, Centre of the Region Haná for Biotechnological and Agricultural Research, Faculty of Science, Palacký University, Šlechtitelů 11, 783 71 Olomouc, Czech Republic
[3]Department of Neurology, University Hospital in Olomouc, I. P. Pavlova 6, 775 20 Olomouc, Czech Republic

E-mail: lubor.urbanek@upol.cz.

Many of the TRP related compounds possess biological or pharmacological properties and their abnormal neurotransmission seems to be linked to a wide range of neurodegenerative and psychiatric diseases. Nevertheless, comprehensive data concerning their physiological roles, human tissue and body fluids levels, as well as the dynamic state of metabolism still remains unclear. The high-throughput UHPLC-MS/MS method was developed for the quantitative analysis of L-TRP and its 16 metabolites in human serum and CSF, covering major and minor routes of L-TRP catabolism. The combination of fast LC gradient and specific tandem mass spectrometry ensured robust analysis of almost 150 samples per 24 h. Due to the better resolution and more narrow peaks in UHPLC analysis, analytes co-eluted negligibly with interferences during ionization. Moreover, the usage of deuterated and $^{13}C^{15}N$-labelled internal standards was confirmed to be ideal, since they showed almost identical behavior to the analytes of interest in sample treatment, chromatography as well as ionization. This gave the unique approach needed to quantify endogenous serum and CSF levels of heterogenous group of compounds spanning a wide concentration range. The study on serum and CSF physiological levels demonstrated reliability of the method that can be useful for large-scale profiling in epidemiological studies.
This research was supported by grant NT/12221 of the Internal Grant Agency of The Ministry of Health of The Czech Republic.

MAE/UHPLC-TOF-MS as a method for determination of carbamazepine and its metabolite in autopsy materials

S. Lendor[1], P. Kościelniak[1], R. Wietecha-Posłuszny[1], A. Woźniakiewicz[1] and M. Zawadzki[2]

[1] Laboratory for Forensic Chemistry, Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Kraków, 3 Ingardena St., 30-060 Kraków, Poland
[2] Department of Forensic Medicine, Wroclaw Medical University, 4 Jana Mikulicza-Radeckiego St., 50-345 Wrocław, Poland

E-mail: aneta.wozniakiewicz@uj.edu.pl

P2-24

The aim of the research was to develop an effective method for determination of carbamazepine (CBZ) and its potential metabolites in human materials obtained at autopsy. Carbamazepine is a pharmacologically active compound with anticonvulsant properties and its structure is related to tricyclic antidepressants such as amitriptyline and imipramine. It is an effective antiepileptic drug (AED) used for the treatment of focal and convulsive generalized epilepsy in humans [1].
The analytical procedure involved sample preparation using the microwave assisted extraction (MAE) in alkaline solution (pH=9.5) with ethyl acetate as the extraction solvent. The microwave process carried out at 80°C for 10 min was found to be the most efficient. Separation of the analytes was performed by ultrahigh performance liquid chromatography coupled with mass spectrometry with time-of-flight detection (UHPLC-MS-TOF) within 5 minutes using Hypersil Gold Phenyl (50x2.1 mm I.D., 1.9 µm) column. The mobile phase consisted of a mixture of 0.1% formic acid in water and of 0.1% formic acid in acetonitrile. Flow rate of mobile phase was 0.4 ml/min and the temperature of column was 25°C.
For the developed and optimized MAE/UHPLC-TOF-MS method precision (<5.4%) and limit of quantification (52.1 pg/mg) were calculated. Finally, the developed method was applied for identification and determination of carbamazepine and its active metabolite – 10,11-carbamazepine epoxide – in tissues post-mortem collected: human hip bone, bone marrow, and hair.

References

[1] P. Petit, R. Lonjon, M. Cociglio, A. Sluzewska, J.P. Blayac, B. Hue, R. Alric, and R. Pouget, *European Journal of Clinical Pharmacology*, 41 (1991) 541-546.

Simultaneous quantitative determination of allergic ingredients in oxidative hair dyes

J.W. Ahn, R.Y. Kim and C.W Park

Cosmetic Research Team, National Institute of Food and Drug Safety Evaluation
Osong-eup, Heungdeok-gu, Cheongju-si, Korea Republic

E-mail: ssjh0203@gmail.com

Recently, consumer side effects occur for example dermatitis, redness, swelling, itching etc. derived from hair dye products.
P-Phenylenediamine(PPD) is a chemical substance that is widely used as a permanent hair dye. It could rise allergy reaction to people while makes more vivid and dark color and improves dyeing force. According to many papers, other major components in oxidative hair dye such as toluene-2,5-diaminesulfate(TDS), m-aminophenol(MAP), σ-aminophenol, p-aminophenol(PAP) also related to allergc contact dermatitis. Since benefit on product value of these components, they are widely used in permanent hair colorants. In order to protect consumer and enhance quality control of hair dyes, establishment of quantitative determination are very important. Several methods have been developed for determination of ingredients in hair dyes. Spectrophotometric detection method such as high-performance liquid chromatography (HPLC) is most often used for the analysis method.
In this study, up to date published analysis methods that simultaneous quantitative determination for more than 5 ingredients has been reviewed with emphasis on HPLC and UPLC. As a result of comprehensive study, appropriate simultaneous quantitative determination for hair dye products has been established.

References

[1] J.P. McFadden and I.R.White *BMJ* (2007)
[2] J.P. Thyssen and A.Linneberg, *Contact Dermatitis*, (2007) 287-299.
[3] L.H.Wang and S.J.Tsai, *Analytical Biochemistry*, (2003) 201-207.
[4] N.A. Penner and P.N. Nesterenko, *Analyst*, (2007) 1249-1254.

Novel bitumen derived stationary phases for gas chromatography

G. Boczkaj, M. Momotko, D. Chruszczyk and P. Makoś

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P2-26

A residuum from vacuum distillation and produced from this stream spectrum of bituminous materials are a complex mixture of hydrocarbons, which are classified on the basis of the so-called group-type composition (SARA) including saturated and aromatic hydrocarbons, resins and asphaltenes. The compounds present in this streams are nonvolatile and have very high thermal stability (up to approx. 380 °C). Separation of these type of complex mixtures into fractions of specific physicochemical properties is possible by selective precipitation and adsorptive column liquid chromatography. A multistage procedure for the separation of fractions from a specified raw material results in a fraction having well-defined physico-chemical properties. Extremely rich structure of the high-molecular compounds isolated from petroleum fractions, constitutes their high potential as the stationary phase with a unique selectivity, particularly steric, as well as their potential chirality.

This paper concerns research on the use of selected fractions isolated from vacuum distillation residuum as stationary phases for gas chromatography. We compared the selectivity of the phases produced using several different methodologies of isolation from different materials for over 50 volatile organic compounds. The size of deviations of the retention expected based on the standards boiling point was examined. Retention indices were compared for the analyzed standards of studied stationary phases with the retention indices obtained for commercial stationary phases, which allowed to determine the McReynolds'a constants and to position the developed stationary phase in a series of selectivity of the current production phases. These studies revealed a high potential of developed phases which exhibit very high selectivity for selected groups of VOC - in particular pyridine and its derivatives.

Acknowledgements: The authors gratefully acknowledge the financial support from the National Center for Research and Development, Warsaw, Poland – Project LIDER, no. LIDER/036/573/L-5/13/NCBR/2014.

Application of monolithic material for determination of iohexol in serum samples by capillary liquid chromatography

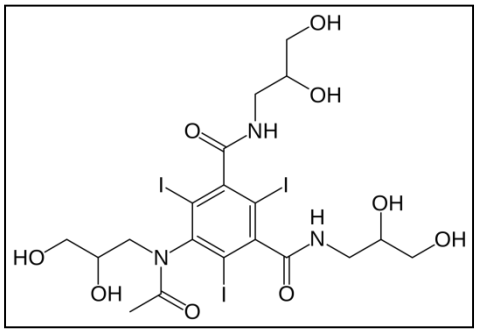
P. Chaisuwan[1,2], T. Chaloemsuwiwattanakan[3], D. Nacapricha[1,4] and P. Wilairat[1,5]

[1]Flow Innovation-Research for Science and Technology Laboratories (FIRST Labs.)
[2]School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand
[3]Department of Chemistry, Faculty of Science, Srinakharinwirot University, Sukhumvit 23 Rd, Bangkok 10110, Thailand
[4] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Rd, Bangkok 10400, Thailand
[5]National Doping Control Centre, Mahidol University, Bangkok, Thailand

E-mail: p.chaisuwan@sut.ac.th

P2-27

Iohexol is currently considered as a standard marker for determination of glomerular filtration rate due to its accurate estimation compared to other markers such as inulin or creatinine [1, 2]. Liquid chromatography is the most common method used for quantitative analysis of iohexol in serum or plasma. To reduce the amount of solvents used in the chromatography, a porous monolithic material was prepared *in situ* in a fused silica capillary (id. 100 µm). Various monomers, polymerisation condition and mobile phase composition were investigated. Good separation in terms of efficiency and peak shape was achieved with chromatographic time of 5 min. This cost effective method was applied for the determination of iohexol in serum samples.



Chemical structure of iohexol (1-*N*,3-*N*-bis(2,3-dihydroxypropyl)-5-[*N*-(2,3-dihydroxypropyl)acetamido]-2,4,6-triiodobenzene-1,3-dicarboxamide).

References

[1] B. Frennby and G. Sterner, *Eur. Radiol*, 12 (2002) 475–484.
[2] E. Brändström,A. Grzegorczyk, L. Jacobsson, P. Friberg,A. Lindahl and M.Aurell, Nephrol. Dial. Transplant, 13 (1998) 1176–1182.

Development of an automated method for methylxanthines determination by gradient–elution flow–injection chromatography

P. Chorti and A. Economou

Department of Chemistry, National and Kapodistrian University of Athens, Athens 157 71, Greece

E-mail: aeconomo@chem.uoa.gr

P2-28

In this work, an automated low–pressure flow–injection chromatography (FIC) instrument was developed. The system consisted of two low–pressure pumps, a 6–way injection valve, a passive mixer, a monolithic separation column and a UV–Vis detector. Synchronized action of the two pumps under computer control enabled the creation of different linear solvent gradients.

The instrument was applied to the determination of 3 methylxanthines (caffeine, theobromine, theophylline). Method development involved the study of: the composition of the mobile phases; the gradient elution protocols; the mobile phase flow rate; the injection volume. Then the method was validated in terms of linearity, dynamic range, limits of detection and determination, repeatability, reproducibility and ruggedness.

Finally, the FIC method was applied to the determination of one or more of the methylxanthines in coffee, tea, drinking chocolate and pharmaceutical tablets. In order to avoid matrix effects, quantification was performed using the multiple standard additions method; recoveries were in the range 90 to 105 %.

Acknowledgements: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS. Investing in knowledge society through the European Social Fund.

Development and validation of a low–pressure chromatography method for the rapid determination of 4 parabens in cosmetic products

M. Barbatsi, P. Chorti and A. Economou

Department of Chemistry, National and Kapodistrian University of Athens, Athens 157 71, Greece

E-mail: aeconomo@chem.uoa.gr

P2-29

This work reports the development of a low–pressure chromatography method for the determination of 4 parabens (methylparaben, ethylparaben, propylparaben and boutylparaben). Separation was performed at a short monolithic separation column and detection was carried out with a UV–Vis spectrometer. The novel feature of the system was the solvent delivery system that consisted of two Milligat® pumps whose synchronized action provided different two–solvent gradient protocols.
A method was developed with optimization of the separation column length, the composition of the mobile phases, the gradient elution profiles and the mobile phase flow rate. Method validation involved study of the linearity, the dynamic range, the limits of detection and quantification, the precision, the trueness and the ruggedness.
The low–pressure chromatography method was applied to the determination of the 4 parabens in cosmetic products (cleaning lotions and hygiene wipes).

Acknowledgements: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS. Investing in knowledge society through the European Social Fund.

Simultaneous capillary electrophoretic analysis of inorganic anions and cations in sweat samples as a novel approach in cystic fibrosis diagnosis

P. Ďurč[1], M. Greguš[1,2], F. Foret[2], J. Skřičková[3], E. Pokojová[3], L. Homola[4], M. Dastych[5], H. Vinohradská[5] and P. Kubáň[1,2]

[1]Department of Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic
[2]Bioanalytical Instrumentation, CEITEC MU, Veveří 97, 602 00 Brno, Czech Republic
[3]Department of Respiratory Diseases and TB, University Hospital Brno, Jihlavská 20, 625 00, Brno, Czech Republic
[4]Cystic Fibrosis Centre, Clinic of Paediatric Infectious Disease, Children´s Medical Center, Černopolní 9, 62500 Brno, Czech Republic
[5]Department of Clinical Biochemistry University Hospital Brno, Jihlavská 20, 625 00, Brno, Czech Republic

E-mail: durc@mail.muni.cz

P2-30

A new approach for diagnosis of cystic fibrosis (CF) is presented. Currently, the gold standard for diagnosis of CF is a sweat test that measures sweat chloride concentration. The sweat of CF patients contains elevated chloride level in comparison to healthy individuals. However, the sweat test is time-consuming and provides many false positive or false negative results. Therefore, a fast and simple sampling technique consisting of wiping the skin of lower side of forearm was developed. The skin wipe samples were analysed by double opposite end injection capillary electrophoresis with contactless conductivity detection (DOEI-CE-C4D). Since there are more markers of CF than only chloride ions (Na^+ and K^+), DOEI-CE-C4D is suitable and fast technique for simultaneous analysis of these ions because of its capability to analyse both cations and anions in one run. By comparing measured ion ratios instead of Cl^- concentrations only, we can better distinguish between healthy individuals and CF patients. When principal component analysis (PCA) is applied to ion ratios, fully separated clusters containing healthy individuals and CF patients are obtained. The data will be presented on sets (n = 10) of healthy individuals, paediatric CF patients and adult CF patients. Partial validation of newly developed method by comparing chloride concentrations in sweat obtained by DOEI-CE-C4D and coulometry used in clinical laboratory was also performed. Developed sampling technique and DOEI-CE-C4D method for multi-ion analysis can be surrogate to standard sweat test in CF diagnostics.

Acknowledgements: The authors acknowledge the financial support from the Grant Agency of the Czech Republic (Grant No. P206/13/21919S). Part of the work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

Novel portable capillary electrophoretic instrument for analysis of very small samples and its application in the analysis of exhaled breath condensate

M. Greguš[1,2], F. Foret[1] and P. Kubáň[1,2]

[1]Bioanalytical Instrumentation, CEITEC Masaryk University, Veveří 97, 602 00, Brno, Czech Republic
[2]Department of Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic

E-mail: gregus@mail.muni.cz

P2-31

Capillary electrophoresis (CE) surpasses others analytical techniques in terms of its high separation efficiency, short analysis time and low consumption of sample and chemicals. Typical CE device consists only of capillary, vessels for BGE with electrodes, detector unit and a high voltage supply. All these parts can be easily miniaturized. Thus portable CE instruments, P-CE, can be easily constructed in contrast to other instrumentation, such as HPLC or MS, respectively. There are many reasons for constructing miniature and portable CE instruments. For instance to reduce degradation and risk of contamination of the samples during the transport and the storage or to obtain the results of analysis immediately at the sampling site. One major technical difficulty in constructing portable CE instruments is the injection part that is either requiring large sample volumes or uses electrokinetic injection that is not suitable for quantitative analysis. In here we present a novel P-CE with a special interface for low-volume sampling able to repeatedly analyze sample volume as low as 20 µL. Moreover, this instrument is constructed for direct sampling of exhaled breath condensate (EBC) from a miniature sampling device, which was developed in our laboratory [1]. EBC is formed by cooling and subsequent process of condensation of exhaled breath. EBC is a promising and interesting liquid sample, which has a potential to be used in clinical research and diagnosis (especially for different respiratory diseases). To this date, there are just few articles, where the EBC was analyzed by CE [1-3]. Analysis of EBC obtained by one, single exhalation is also possible by this instrument. The developed instrument is however not limited only to EBC, but samples of different origin and amount can be analyzed too. Construction, technical details and characterization of developed P-CE are discussed.

Acknowledgements: The authors acknowledge the financial support from the Grant Agency of the Czech Republic (Grant No. P206/13/21919S). Part of the work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

References

[1] M. Greguš, F. Foret and P. Kubáň, *Electrophoresis*, 36 (2015) 526-533.
[2] P. Kubáň, E-G Kobrin and M. Kaljurand, *Journal of Chromatography A*, 1267 (2012) 239-245.
[3] M. Greguš, F. Foret, D. Kindlová, E. Pokojová, M. Plutinský, M. Doubková, Z. Merta, I. Binková, J. Skřičková and P. Kubáň, *Journal of Breath Research*, 9 (2015) accepted.

A new capillary electrophoretic method for determination of oxidized and reduced glutathione in non-invasively acquired biological samples

J. Hodáková[1], J. Preisler[1], F. Foret[2] and P. Kubáň[1,2]

[1] Department of Chemistry, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic,
[2] Bioanalytical Instrumentation, CEITEC MU, Veveří 97, 602 00 Brno, Czech Republic

E-mail: juliahod@gmail.com

P2-32

Reduced glutathione (GSH) is one of the most significant components of the collective antioxidant defences [1]. By reacting with radicals and oxygen-reactive species, it fulfils a major role in protecting the cells and tissue structures.Decrease in GSH level and increase in oxidized form (GSSG) level orlowering of the GSH/GSSG ratio are considered to be important indicator of a number human diseases [2].Non-invasively acquired samples are promising in clinical diagnosis and could replace the invasive samples such as blood or blood serum, but often the concentration of biomarkers in these samples is low. For instance, in saliva, the concentration of GSH is in the µM range, but only nM concentration of GSH are present in an attractive,non-invasive, diagnostic sample - exhaled breath condensate (EBC).A new sensitive capillary electrophoretic method with laser-induced fluorescence (LIF) was developed for sensitive determination of oxidized and reduced glutathione in non-invasive samples.For derivatization of GSHa fluorescent tag eosin-5-maleimide (EMA) was used. The formed complex, GSH-EMA, was detected with an in-house built CE-LIF system with 515 nm diode laser module. The GSSG was reduced with tris(2-carboxyethyl)phosphine (TCEP), resulting in two reduced GSH molecules that were tagged with EMA and detected. In this work separation conditions,derivatization process of EMA with and without reducing agent and reduction conditions of TCEP were optimized and a novel CE-LIF method with sub-nM concentration sensitivity for GSH and GSSG is presented.

Acknowledgements: The authors acknowledge the financial support from the Grant Agency of the Czech Republic (Grant No. P206/13/21919S). Part of the work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

References

[1] N. Maeso, D. Garcia-Martinez, F.J. Rupérez, A. Cifuentes and C. Barbas, *Journal of Chromatography B*, 822 (2005) 61-69.
[2] Y. Iwasaki, M. Hoshi, R. Ito, K. Saito and H. Nakazawa, *Journal of Chromatography B*, 839 (2006) 74-79.

C-reactive protein in viral and bacterial infections

R.F. Măties

Faculty of Chemistry and Chemical Engineering,
Babeş-Bolyai University, str. AranyJános nr. 11, 400028, Cluj, Romania

E-mail: raluca_maties@yahoo.com

P2-33

C-reactive proteinis produced by the liver and secreted into the blood. This can be measured by two different tests: the test CRP and high-sensitivity CRP test (hs-CRP), each measuring different ranges of testing CRP levels in the blood [1-3].
CRP values increase in the presence of inflammation and infection, and following a myocardial infarction (heart attack) after surgery andpost-trauma. Therefore, CRP is one of a number of proteins, which are also known as a cute phase reactants, which are used to monitor the development of inflammation associated with many autoimmune diseases and infectious diseases [4-5].
This paper examines a set of recent data collected in a specialized laboratory in Cluj, following extent that CRP values correlate with various pathologies involved, focusing on differentiation of the bacterial versus viral conditions, or other major groups detected in that group.

References

[1] Laborator Synevo, http://www.synevo.ro/proteina-c-reactiva-inalt-sensibila-hscrp/
[2] F. Araújo, A.C. Pereira, M. Do Rosário, D.O. Latorre, J.E. Krieger and A.J. Mansur, *International Journal of Cardiology*, 97 (2004) 433-438.
[3] F. Araújo, I. Antelmi, A.C. Pereira, M. Do Rosário, D.O. Latorre, C.J. Grupi, J.E. Krieger and A.J. Mansur, *International Journal of Cardiology*, 107 (2006) 333-337.
[4] M.S. Koren, J.Q. Purnell, P.A. Breen, C.C. Matthys, H.S. Callahan, and D.S. Weigle, *Nutrition*, 22 (2006) 444-448.
[5] S. Zhang, Q. Liu, J. Wang and D.C. Harnish, *Biochemical and Biophysical Research Communications*, 379 (2009) 476-479.

Chiral amino acid ester-based ionic liquids: Their utility as additives in capillary electrophoresis for improved chiral separations

M.C. Mavroudi and C.P. Kapnissi-Christodoulou

University of Cyprus, Department of Chemistry, Nicosia, Cyprus

E-mail: mavroudi.c.maria@ucy.ac.cy

P2-34

In this study, the utility of amino acid ester-based ionic liquids (AAILs) as additives in mobile phases for improved chiral separations in capillary electrophoresis (CE) was investigated. In particular, L-Alanine *tert* butyl ester Lactate (L-AlaC_4Lac) was synthesized and then added into the mobile phase in order to improve the chiral separation of different analytes in regard to efficiency (N) and resolution (R_s). Parameters, such as the concentration of the chiral selector and the AAIL, and buffer pH, were systematically examined in order to optimize the chiral separation of each analyte. It was observed that the addition of the AAIL into the BGE improved both resolution and efficiency significantly. In addition, these last two key parameters were compared before and after the use of the additive in order to demonstrate the importance of chiral AAILs in CE for more efficient chiral separations.

Determination of boiling point distribution by means of chromatographic techniques - standard test methods and new developments

M. Momotko, D. Chruszczyk, P. Makoś and G. Boczkaj*

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P2-35

Boiling point distribution (BPD) is an important parameter determined especially for petroleum fractions and products. Provides a valuable source of information on the properties of crude oil and the content of each fraction, as well as the optimal operating conditions of the atmospheric or vacuum distillation [1].
Currently, the BPD is determined alternatively by classic distillation or simulated distillation (SIMDIS). The SIMDIS is described in several dedicated standard test methods and uses gas chromatography technique (GC). The BPD is determined from the GC-FID chromatogram, on the basis of retention time - the boiling point calibration made for the n-alkanes. SIMDIS is a method well-mastered for light petroleum products. However, in the case of vacuum distillates, batch streams for hydrocracking process or vacuum residues, many problems occur due to the high temperature of the final part of the separation. Determination of the final boiling point (FBP), which is a very important parameter, is difficult when the temperature of chromatographic separation in GC is up to 450°C. Unfavorable affects take place mainly the increase of the background signal and the partial thermal decomposition of less stable components of the sample.
This paper presents a comparison of SIMDIS methods and new developments in this field including an Empty Column Gas Chromatography (EC-GC) [2-3] and Size Exclusion Chromatography with Refractive Index Detector (SEC-RID) [4]. EC-GC conditions are based on empty deactivated fused silica column which better "simulate" the distillation process. SEC-RID is an interesting alternative to GC, where size exclusion conditions are used to separate hydrocarbons according to their molecular mass and correlate the retention data with their boiling point.

References

[1] M. Momotko and G. Boczkaj, *Przem. Chem.* 2015.
[2] G. Boczkaj, A. Przyjazny and M. Kamiński, *Anal. Bioanal. Chem.*, 399 (2011), 3253-60.
[3] G. Boczkaj and M. Kamiński, *Anal. Bioanal. Chem.*, 405 (2013), 8377-8382.
[4] G. Boczkaj, A. Przyjazny and M. Kamiński, *J. Sep. Sci*,. 38 (2015), 741-748

Multi-applicational character of silanized silica gel as stationary phase for gas chromatography

M. Momotko, P. Makoś, D. Chruszczyk and G. Boczkaj

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P2-36

Most of the applications of silica gel is connected with liquid chromatography. Some simple separations of permanent gases are known as gas chromatographic applications using pure SiO2. The silanized silica gel (Sil-SiO2) is commercially available and due to the surface hydrophobization has a unique and interesting properties which could be used in gas chromatography.

This paper describes a research on separation properties of silanized silica gel for gas chromatography. A commercially available sorbent was sieved to achieve a 80/100 mesh particle fraction, which was used to prepare a 1/8" ID packed column. The column was used for separation of permanent gases, light hydrocarbons and several groups of volatile organic compounds (VOCs). As a result of silanization, the Sil-SiO2 should be almost inert to separated solutes, thus the elution order of compounds is expected to be easily correlated with their boiling point values [1-3]. Due to that reason the Sil-SiO2 was also examined as a stationary phase for simulated distillation applications.

The studies revealed, that in the case of permanent gases Sil-SiO2 has a similar separation properties as pure silica gel, but it is also suitable to separate more polar compounds normally strongly adsorbed on SiO2 like carbon dioxide and water. Separation of normal paraffins is possible in the range of C1 to C24 using temperature program. The complete separation takes places even when the initial temperature of separation is above 60°C. This allows to analyze light petroleum streams without the need of cooling the GC oven below the ambient temperature. Studies in the SIMDIS conditions proved that Sil-SiO2 column is suitable for boiling point distribution determination of gasoline and diesel oil samples.

References

[1] M. Momotko and G. Boczkaj, *Przem. Chem.*, 2015.
[2] G. Boczkaj, A. Przyjazny and M. Kamiński, *Anal. Bioanal. Chem.*, 399 (2011), 3253-60.
[3] G. Boczkaj, M. Kamiński and *Anal. Bioanal. Chem.*, 405 (2013), 8377-8382.

Application of hydrophilic interaction liquid chromatography (HILIC) in the separation and analysis of cathinone regio-isomers using HPLC

E.Y. Santali[1], D.G. Watsona and O.B. Sutcliffe[2]

[1] Strathclyde Institute of Pharmacy and Biomedical Science SIPBS, University of Strathclyde, Glasgow, G4 0NR. UK
[2] School of Science and the Environment, Manchester Metropolitan University, Manchester, M5 1GD. UK

P2-37

Introduction: **(±)**4-Methylmethcathinone, or (±)Mephedrone, is a synthetic beta-ketoamphetamine that is currently controlled in the United Kingdom as a Class B, Schedule 1 substance under the Misuse of Drugs Act (1971). It occurs in 3 regio-isomeric forms with different chromatographic profiles, thus posing significant challenges to forensic analysts engaged in routine screening of seized or toxicological samples. A GC-MS method for assay of these regio-isomers has been reported previously. We report here the development of a liquid chromatographic method for the detection of theseregio-isomeric forms in mephedrone samples.
Methods: Samples were run on three HILIC columns: CN-Zorbax (150x3mm, 3µm), Cogent Silica Hydride (150x4.6mm, 3µm) and CN-ACE (250x4.6mm, 3µm) columns. The mobile phase consisted of95:5 acetonitrile/0.6 mM ammonium acetate pH≈6, flow rate 1mL/min and UV detection at 258 nm.
Results: Baseline resolution was reproducibly attainedfor all threeregio-isomers on Cogent silica hydride column in a reasonable runtime(6-10 min) with good precision (%RSD<0.9%, n=6), linearity (R^2=0.999) and chromatographic efficiency (N=80-100K, H=0.9-1.25x10^{-5}plates $metre^{-1}$).An unexpectedintense andearly-eluting peak (RT 0.81min) appeared in the chromatogram during repeated injections of the sample, followed by gradual degradation of the2-Methylmethcathinone (2-MMC) peak. The degradation profile approximated to first order kinetics (R^2>0.995) with a decay constant of 3.433x10^{-3} min^{-1}, givinga half-life ($t_{0.5}$) of ~201.9 min (3.4 h) and $t_{0.9}$ of 30.7 min (0.51 h).However, analysis by NMR did not show the degradation product to be different from the 2-MMC parent compound. LC-MS analysis showed a loss of just two hydrogen atoms from the parent molecule.
Conclusion: A fast and reproducible method for the analysis of mephedrone region-isomers has been developed. The stability of 2-MMC needs to be further investigated in order to determine the most appropriate run conditions that would keep it stable for a longer time during the assay.

Modern Separation of Liposolubile Vitamins in Clinical Research

D. Solichová[1], L. Kujovská Krčmová[1,2], J. Plíšek[2], J. Aufartová[1,2], E. Kasalová[1,2], B. Honegrová[2] and P. Solich[2]

[1]III. Internal Gerontometabolic Clinic, University Hospital Hradec Králové, Sokolská 581, 500 05 Hradec Králové, Czech Republic
[2] Department of Analytical Chemistry, Faculty of Pharmacy, Charles University, Heyrovského 1203, 500 05 Hradec Králové, Czech Republic

E-mail: solich@lfhk.cuni.cz

P2-38

High performance liquid chromatography is one of the most progressive separation techniques which allows identification and quantification in one step and is frequently used in clinical research for analysis of biological samples in connection with modern sample preparation method. Choice of the sample preparation technique is key step which influence sensitivity, robustness, solvents, sample consumptions etc. Connection of modern, fast and robust sample preparation procedures with recent trends in liquid chromatography is useful base for clinical research.
In this study various modern sample preparation techniques in combination with ultracentrifugation, HPLC or UHPLC, and new stationary phases such as core shell, sub 2-µm and monolith technology for separation of vitamin A, E and D in different biological materials (serum, lipoprotein fractions, and breast milk) used in the Research Laboratory of III. Internal Gerontometabolic Clinic at University Hospital Hradec Králové Czech Republic will be presented:

a) The fast analysis of tocopherols and retinoids in various biological materials achieved by utilization of the first and second generation of monoliths (Chromolith Performance C18-e, High Resolution Chromolith Performance, Merck) with good selectivity and specificity[1, 2]
b) New UHPLC-MS/MS method for determination of 25-OH D_2 and 25-OH D_3 in serum and breast milk using core shell column Kinetex (Phenomenex) and microplates technology for monitoring of vitamin D status [3]
c) New method for determination of alpha tocopherol in human erythrocytes which combines ultracentrifugation and SPE for sample preparation [4].

Acknowledgements: This work was supported by grants of IGA Ministry of Health Czech Republic, No. NT/13564-4/2012, NT/13566-4/2012 and NT/14265-3/2013.

References

[1] L. Urbánek, D. Solichová, B. Melichar et al., *Analytica Chimica Acta*, 573 (2006) 267-272.
[2] B. Kucerova, L. Krcmova, D. Solichova et al., *Journal of Separation Science*, 36 (2013) 2223-2230.
[3] J. Plíšek, L. Krčmová, J. Aufartová et al., *Journal of Separation Science*, 36 (2013) 3702-3708.
[4] J. Plíšek, N. Pospichalova, M. Khalikova et al., *Journal of Separation Science*, 38 (2015) 634-640.

An improved QSAR model for explaining the blood–brain barrier permeability mechanisms

R. Aalizadeh and N.S. Thomaidis

Laboratory of Analytical Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Panepistimiopolis Zografou, 15771 Athens, Greece

E-mail: ntho@chem.uoa.gr

P2-39

Blood-brain barrier (BBB) is a physiological barrier that separates the bloodstream and brain tissue and plays a major role in maintaining brain homeostasis. BBB is comprised of endothelial cells which constitute the cerebral micro-vessels. Thus, BBB is a physical and metabolic barrier which is responsible for drug to central nervous system (CNS) transportation. The ability of compound to penetrate through BBB can be estimated by calculating its blood to brain distribution (log BB). Permeability of BBB is one of the most important factors in drug design not only for increasing the biological responses of drugs targeting receptors inside BBB, but also a good tool for studying the side effect of drugs not targeting CNS. Performing the experiments for analysis of drug permeability is time consuming, expensive and yet complicated, and therefore, a fast and validated method is highly required. Several approaches based on QSAR were developed; however, the results and their applicability domain were not adequate [1]. In this work, we developed an internally and externally validated QSAR model using kNN-GA-MLR based on 85 compounds (training and test set) to study the mechanism of permeability of BBB of some compounds and then kNN-GA-SVM method was employed to predict the end points accurately. Chemical structures of taken compounds were optimized using Density Functional Theory (DFT) / B3LYP with the biases of 6-31G* and then Dragon program was used to derive the molecular descriptors. LogD at pH= 7.4 and LogP were also calculated and amended to the dataset for variable selection step by genetic algorithm. Consensus modelling and Kohonen self-organizing maps were used to prevent any information lost during division of data set. Monte Carlo sampling, William plots coupled with Cook's distance and Euclidean based applicability domain were employed to study the origin of outliers in proposed models. The results indicated that Radial Distribution Function 105/weighted by atomic mass, R autocorrelation of lag 4 and 3D-MoRSE descriptor signal 03 weighted by Sanderson electronegativity would lead to increase of logBB values of compounds, and H attached to C0 (sp3) with 1X attached to next C, presence/absence of C-O, N-N and Frequency of F - F at topological distance 2 and 3D-MoRSE descriptor signal 19 / weighted by atomic mass would decrease the logBB values.

Table 1. The statistical results of the proposed models

	Training set					Test set				
	R^2	RMSE	CCC	Q^2_{LOO}	F	R^2	RMSE	CCC	R^2_m	F
kNN-GA-MLR	0.812	0.1840	0.896	0.744	31.42	0.850	0.213	0.882	0.731	2.628
Cons. Model	0.820	0.1860	0.892	0.743	--	0.851	0.208	0.890	0756	--
kNN-GA-SVM	0.920	0.1247	0.953	0.700	70.58	0.867	0.201	0.900	0.825	3.331

References

[1] R. Bujak, W. Struck-Lewicka, M. Kaliszan, R. Kaliszan and M. J. Markuszewski, *J Pharm Biomed Anal*, 108 (2015) 29–37

Magnetic solid phase extraction based on magnetic hypercrosslinked polystyrene for determination of tetracycline antibiotics in waters with HPLC

V.V. Tolmacheva, E.V. Kochuk, V.V. Apyari and S.G. Dmitrienko

Chemistry Department of Lomonosov Moscow State University, Leninskie gory, 1/3, 119991 Moscow, Russia

E-mail: nikatolm@mail.ru

P2-40

Magnetic solid phase extraction (MSPE) is a new version of SPE based on sorption of target analytes on magnetic sorbents that can be readily isolated from sample matrix by applying external magnetic field. Compared with traditional SPE procedure, MSPE is more rapid, inexpensive and easy to handle. The MSPE separation process can be performed directly from unpurified samples containing suspended solid material without the need of additional centrifugation or filtration. The MSPE adsorbents can be uniformly dispersed in sample solution by stirring or shaking, which makes the contact area between the adsorbent and the analytes large enough to ensure fast mass transfer and allow for achieving high extraction efficiency in a short time.

In our opinion, hypercrosslinked polystyrene (HCP) due to its high specific surface area (>1000m^2/g) and high percentage of micropore has a great potential in sorption processes. The imparting magnetic properties to HCP can combine the high adsorption capacity of HCP and the separation convenience of magnetic materials.

In this work, a HCP-based magnetic absorbent was synthesized by simple adsorption of pre-synthesized Fe_3O_4 nanoparticles onto HCP. The resultant material was used as a MSPE adsorbent for the preconcentration of four tetracyclines from natural water and their determination with high-performance liquid chromatography with an amperometric detector.

Four magnetic adsorbent samples were synthesized, and their structural, magnetic and sorption properties were studied. Conditions of the magnetic adsorbents synthesis were optimized by varying the weight of HCP and the content of Fe_3O_4. Parameters of porous structure of the adsorbents and their specific surface areas were determined by the nitrogen adsorption at low temperature. Microstructure of the samples was investigated by scanning electron microscopy. The magnetization curves of the materials were also measured. To achieve the best extraction efficiency, various conditions, such as amount of the adsorbent, pH, extraction time, desorption time and the nature of an eluent, were optimized. Sorption properties of HCP, magnetic HCP, and magnetic nanoparticles regarding tetracycline, oxytetracycline, chlortetracycline and doxycycline were compared. It has been shown that the HCP-based magnetic adsorbent retains sorptive properties regarding tetracyclines (R = 95 – 97%) and can be easily separated from solution by applying magnetic field. The magnetic HCPs were applied for group preconcentration of tetracycline antibiotics from river water samples followed by HPLC determination.

Acknowledgements: This work was financially supported by the Russian Foundation for Basic Research (grant N 13-03-00100_a)

Optimization of a RP-HPLC/UV-Vis technique for the separation of the individual heavy and light rare earths from red mud after selective extraction/backstripping processes

L.-A. Tsakanika and M. Ochsenkühn-Petropoulou

Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, NTUA

E-mail: btsakanika@gmail.com, oxenki@central.ntua.gr

P2-41

The last years rare earths (REEs) scandium (Sc), yttrium (Y) and lanthanides (Lns) are referred as critical elements because of their numerous uses in high-tech applications. Despite their great demand, their supply remains low due to the few economic and easily exploitable REEs resources (the "balance problem"), leading to their high values especially as individual elements of high purity. Red mud (RM), the alkaline residue of alumina's production from bauxites is enriched in REEs and other trace elements of industrial importance. For Greek RM an over 20 years investigation has shown that it contains 130g Sc/ton RM and ~1kg REEs/ton RM [1,2]. Thus, it could be used as an alternative low cost resource of REEs, contributing also to partial utilization of bauxite waste whose accumulation in recent years has increased rapidly. For the separation and purification of REEs, chromatographic and selective extraction techniques are the most widely used both in lab and industrial scale.

In the present work the optimization of a reversed phase (RP) HPLC technique for the separation of the individual heavy and light REEs after their recovery in two groups by selective extraction/backstripping processes with suitable agents, is presented. The study is based on our previous investigation of REEs chromatographic separation from RM [3] after an innovative multi process method for RM utilization including acid leaching, ion exchange, extraction/backstripping, developed in our lab and scaled up to a pilot plant [2,4,5,6]. However a co-elution between Y/Dy and Nd/Pr was observed [3]. The proposed separation is achieved on a RP C18 AQ column modified with octanosulfonic sodium salt applying suitable gradient elution profiles of four eluents. For the determination post-column derivatization with PAR and UV-Vis detection were applied. The method was tested and optimized on synthetic aqueous REEs mixtures and real samples from RM utilization procedure as well as on simulated matrix solutions of HREEs and LREEs after the backstripping processes. By using the optimized technique both HREEs and LREEs can be separated with very good resolutions (Rs) even for the pairs Y/Dy and Nd/Pr, lower detection limits and good repeatability.

References

[1] M. Ochsenkühn-Petropulu, T. Lymperopulu and G. Parissakis, *Anal Chim Acta*, (1994) 296 305-313.
[2] L.-A. Tsakanika (2013) PhD thesis, School of Chemical Engineering, NTUA.
[3] L. Tsakanika, M. Ochsenkühn-Petropoulou and L. Mendrinos, *Anal Bioanal Chem*,. (2004) 379 796-802.
[4] M. Ochsenkühn-Petropulu, T. Lyberopulu, G. Parissakis, *Anal Chim Acta*, (1995) 315 231-237.
[5] M. Ochsenkühn-Petropoulou, K. Hatzilyberis, L. Mendrinos, C. Salmas, *Ind. Eng. Chem. Res.*, (2002) 41 5794-5801.
[6] M. Ochsenkühn-Petropoulou, L.-A. Tsakanika, T. Lymperopoulou, Proceed. ERES 2014-1st International Conference on European Rare Earth Resources (2014).

Efavirenz determination in samples obtained in transport studies using HPLC with UV detection

L. Zelena[1], J. Reznicek[2], M. Ceckova[2] and H. Sklenarova[1]

[1]Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, AkademikaHeyrovskeho 1203, 500 05 Hradec Kralove, Czech Republic
[2]Department of Pharmacology and Toxicology, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, AkademikaHeyrovskeho 1203, 500 05 Hradec Kralove, Czech Republic

E-mail: zelenal@faf.cuni.cz

P2-42

The aim of this experimental work was to develop a high-performance liquid chromatography (HPLC) method with simple sample pre-treatment step for efavirenz determination in OptiMEM® Reduced Serum Medium and apply this method to analysis of real samples obtained in studies of transcellular drug transport of efavirenz.

Efavirenz (EFV), a non-nucleoside reverse transcriptase inhibitor, is a drug used in a pharmacotherapy of HIV-positive patients. Transport studies on cellular monolayers grown on cell culture inserts are used to evaluate drugpermeability and to assess possible drug interactions with membrane transport proteins in vitro.

Two facts were considered during sample pre-treatment step: complex sample matrix (cells were cultivated in OptiMEM® Reduced Serum Medium containing nutrients, growing factors, etc.) and low sample volume (50 µL only). Due to this, common techniques as protein precipitation, liquid-liquid extraction or solid phase extraction were not possible to be used. Sample filtration through syringe filters made of different materials with pore size of 0.2 µm accelerated by centrifugation was tested, but loss of EFV was observed. Finally, dilution with internal standard solution (1:1, v/v) and direct sample injection into analytical column with high pore size (5 µm) was chosen.

HPLC method was optimized, validated and used for real sample analyses. HPLC system Nexera X2 with PDA detector (Shimadzu Corporation, Japan) and analytical column Discovery HS C18 (150 x 4.6 mm, 5 µm, Supelco, USA) were used. β-Estradiol 17-acetate was applied as an internal standard. Injected sample volume was 10 µL. Mobile phase consisted of acetonitrile and ultrapure water (65:35, v/v). Analysis was performed at the flow rate of 1.6 ml/min at the temperature of 25°C and took 5 min. UV detection was set to 245 nm.

The method was linear in the concentration range of 0.5-10 µmol L^{-1} (R^2=0.9985) with LOD 0.15 µmol L^{-1} and LOQ 0.5 µmol L^{-1}. Repeatability of peak area (RSD %, n=8) was 1.06 %, 2.35 % and 2.77 % for concentrations of 10, 2.5 and 1 µmol L^{-1}, respectively. Standard addition method applied on real samples showed recovery 99-102 % (n=6).

Acknowledgements: The study was supported by the project of specific research, SVV no. 260 184.

Development and validation of HPLC methods for the determination of amino acids in pharmaceutical formulation based on precolumn derivatization and Vis detection and ion-exchange separation and chemiluminescence detection

D.C. Tsikna, A. Economou, M. Koupparis

Department of Chemistry, National and Kapodistrian University of Athens, Athens 157 71, Greece

E-mail: koupparis@chem.uoa.gr

P2-43

Amino acids play a significant role in human health and several pharmaceutical products containing mixtures of amino acids are administered to patients. The analytical challenge in this case is the difficulty for the determination of all amino acids.

In this work the development and validation of an HPLC method for the determination of 15 amino acids in a pharmaceutical preparation based on pre-column derivatization with dabsyl chloride, separation with a C_{18} column and Vis spectrophotometric detection is described. Extensive optimization of the experimental parameters for derivatization (pH, time, reagent concentration) and for separation was carried out.

Another HPLC method has been developed based on ion-exchange separation of amino acids and chemiluminescence detection based on several reactions. The characteristics of the two methods are compared and discussed.

European Union
European Social Fund

OPERATIONAL PROGRAMME
EDUCATION AND LIFELONG LEARNING
investing in knowledge society
MINISTRY OF EDUCATION & RELIGIOUS AFFAIRS, CULTURE & SPORTS
MANAGING AUTHORITY

NSRF 2007-2013
programme for development
EUROPEAN SOCIAL FUND

Co- financed by Greece and the European Union

This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: THALIS. Investing in knowledge society through the European Social Fund.

Fat droplets characterization of synthetic milk emulsions at various casein concentrations (Cas), by the SdFFF method

A. Vagena[1]. G. Karaiskakis[1], J. Kapolos[2], A. Koliadima[1]

[1]Chemistry Department, University of Patras, 26504 Patras Greece
[2]Food Technology Department, Technological and Educational Institute of Peloponnese, 24100 Kalamata Greece

E-mail: akoliadima@upatras.gr

P2-44

Field-Flow Fractionation (FFF), is a relative new and innovative one phase chromatographic technique. FFF applied in order to analyze, separate and characterize particles with sizes from about 1 nm to more than 100 μm. This technique, introduced by J. C. Giddings in 1966, and till know has been developed by using various external fields (electrical potential differences, temperature gradient, centrifugal or gravitational etc) as stationary phase and different solvents as mobile phase covering a wide range of applications.
The aim of the present study refers to the characterization of fat droplets, in a very important emulsion, milk, by using the Sedimentation Field Flow Fractionation, (SdFFF). In this sub-technique of FFF the centrifugal uses as external field, acting perpendicular to the movement of the carrier solute.
Milk, an emulsion of two or more immiscible liquids, is a natural product which appears in different compositions and components concentrations. These differences are responsible for the variety of nutritional and physicochemical characteristics among many milk products. Proteins are of the most important components of the milk, because enhance the energy content and at the same time contribute to the emulsion stability. The casein protein family, is one of the most important natural emulsifier, because of their high abundance in many food products. Caseins in milk, contain the 80 % of the total protein amount. Because of that casein concentration was studied as parameter for the stability of synthetic milk which contains 15 % (w/w) corn oil in water. The produced emulsions characterized by the SdFFF technique, and the weight average particle size distribution (d_w) of fat droplets as well as their dispersion were calculated. From the results the optimum value for casein in order to produce stable emulsions was found.

Wednesday 23 September 2015

Royal Cruise Hall-A

Chair: B. Michalke, A. Pappa

Chromatography 1

Invited lecture

Comprehensive two dimensional Liquid Chromatography – Coming of age ?

E. Rosenberg

Vienna University of Technology, Institute of Chemical Technologies and Analytics
Getreidemarkt 9/164 AC, A-1060 Vienna, Austria

E-mail: E.Rosenberg@tuwien.ac.at

IL14

Comprehensive two-dimensional chromatography in the liquid phase has been around for more than 50 years now in the form of comprehensive 2D-thin layer chromatography (2D-TLC) [1]. The instrumental version of this technique, comprehensive 2-dimensional HPLC or LCxLC, however, took surprisingly long to establish itself as an important contribution to the analytical toolbox. While GCxGC was quickly embraced by the analytical community, the lack of commercially available instrumentation solutions, together with the significant difficulties of implementing LCxLC has delayed its widespread use until very recently [2].
The commercial introduction of reliable and pre-configured systems for comprehensive 2D-HPLC, together with a better understanding of the processes that have hampered achieving a high peak capacity on these systems before, eventually have changed the situation [3].
Although the operation of a LCxLC system has still to be considered far more sophisticated than that of comprehensive two-dimensional GC systems, the technique is finding an increasing number of followers, and also a growing number of applications [4].
In this presentation, the critical factors for the success of comprehensive 2D-LC will be reviewed and discussed, and suggestions derived for their optimization. Particular consideration will be given to close the gap between the theoretical limits of peak capacity of this technique, and the currently achieved values. Also, a critical comparison of the best achievable separation in one- and two-dimensional chromatography will be made.
Various examples will be taken particularly from the field of food and environmental analysis to illustrate the author' views. They will not only demonstrate the need, but also the benefits arising from the use of comprehensive two-dimensional liquid chromatography.

References

[1] W.D. Skidmore, C. Entenman, *J. Lipid Res.*, 3 (1962) 471-475).
[2] L. Mondello, A.C. Lewis, K.D. Bartle, *Multidimensional Chromatography*. Wiley, New York (2001).
[3] F. Bedani, P.J. Schoenmakers, H.-G. Janssen, *J. Sep. Sci.*, 35 (2012) 1697–1711.
[4] D. Li, C. Jakob, O. Schmitz, *Anal. Bioanal. Chem*. 407 (2015), 153-167.

.

Potential of capillary electrophoresis in clinical diagnosis and monitoring

P. Kubáň

[1] Bioanalytical Instrumentation, CEITEC Masaryk University, Veveri 97, 602 00 , Brno, Czech Republic

E-mail: petr.kuban@ceitec.muni.cz

WE01

Clinical diagnosis and monitoring can greatly benefit from the latest advances in analytical chemistry, most notably the development of microcolumn separation techniques. Capillary electrophoresis (CE) is a fast separation technique that can handle very small sample volumes and is potentially suitable for analysis of clinical samples, obtained either invasively (blood, cerebrospinal fluid, sputum, etc.) or non-invasively (urine, saliva, sweat, exhaled breath condensate). CE is also easily miniaturized and can be potentially used in mobile laboratories and point-of-care diagnostics. The interdisciplinary collaboration of physicians and analytical chemists can result in original and new insights into several diagnostic methods. In this contribution, some of the recent advancements will be presented with emphasis on analysis of metabolites in very small volumes of various biological fluids. A recently developed, fast and simple CE method with contactless conductometric detection for monitoring metabolites during methanol poisoning will be presented, with several real cases studied during the in 2012-13 in the Czech Republic [1]. A potential for monitoring of patient's status during haemodialytic treatment will also be discussed. Further the diagnostic potential of CE will be demonstrated on analysis of exhaled breath condensate in monitoring of various respiratory tract diseases, including asthma, chronic obstructive pulmonary disease and cystic fibrosis [2]. Selected examples of application of CE either with contactless conductometric detection (C4D) or laser induced fluorescence (LIF) will be discussed. Additionally a novel approach in diagnosing cystic fibrosis (CF) and monitoring the CF therapy progression, based on CE analysis of ionic content of sweat and application of chemometrics (PCA) will be discussed [3] and the latest promising results from our laboratory will be shown.

Acknowledgement

The financial support from the Grant Agency of the Czech Republic (Grant No. P206/13/21919S) is acknowledged. Part of the work was realized in CEITEC - Central European Institute of Technology with research infrastructure supported by the project CZ.1.05/1.1.00/02.0068 financed from European Regional Development Fund.

References

[1] P. Kubáň, F. Foret and R. Bocek, *J. Chromatogr. A*, 1281 (2013) 142-147.
[2] M. Greguš, P. Kubáň and F. Foret, *Electrophoresis*, 36 (2015) 526-533.
[3] P. Kubáň, M. Greguš, E.Pokojová, J. Skřičková and F. Foret, *J. Chromatogr. A*, 1358 (2014) 293-298.

Cadmium and mercury speciation in water hyacinth using HPLC-ICP-AES based approach

T.E. Romanova[1,2], O.V. Shuvaeva[1,2]

[1]Nikolaev Institute of Inorganic Chemistry, Academician Lavrent'ev Ave, 3, Novosibirsk, 630090, Russia
[2]Novosibirsk State University, 2 Pirogova Str., Novosibirsk, 630090, Russia

E-mail: romanova-toma@mail.ru

It is well known that the plants are capable to hyperaccumulation [1] but despite their extensive use for water cleaning in environment the essence of this phenomenon remains unclear. So the problem associated with the study of elements transformation and transport inside the plants [2] is of current interest. Special attention is paid to the development of hyphenated systems the selectivity of which with respect to certain species is provided by pre-separation in combination with the subsequent detection of individual species using element selective detectors.

In present work authors suggested an approach for identification of cadmium and mercury species in water hyacinth which is based on the analytes extraction followed by their HPLC separation with UV and element-selective detection and determination of amino acids and thiol groups in the isolated fractions. The optimal parameters for the interfacing of microcolumn chromatograph and ICP-AES have been developed. On the example of the synthesized model compounds of mercury and cadmium with cysteine and glutathione, which can be produced in plants, applicability of HPLC-ICP-AES method for identification of pollutants' species in plants was studied. It has been shown as a result that cadmium and mercury containing compounds can be attributed to peptides similar to phytochelatins.

In contrast to the traditional "black box" cosiderations, investigations of contaminant speciation in plant tissues have given sound understanding of the phytoremediation phenomenon. Such advancements could provide a basis for future improving the efficacy of the biological remediation processes.

This work was supported by the Russian Foundation for Basic Research [№ 14-03-31971].

References

[1] C.D. Jadia and M.H. Fulekar *Afr. J. Biotechnol.*, 8(6) (2009) 921–928.
[2] O.V. Shuvaeva, L.A. Belchenko and, T.E. Romanova *Int. J. Phytorem.*, 15 (2013) 979-990.

Measurement of acid-soluble aldehydes and alcohols derived from lignin using HPAEC-PAD

N. Anders[1], H. Humann[1] and A. C. Spieß[1,2]

[1] AVT-Enzyme Process Technology, RWTH Aachen University, Aachen, Germany
[2] DWI – Leibniz Institute for Interactive Materials, Aachen, Germany

E-mail: nico.anders@avt.rwth-aachen.de

The declining amount of fossil resources results in a change in the view in the chemical industry. New sustainable processes need to be developed in order to produce Green Chemicals or Bio-Fuels. However, the usage of renewable resources instead of fossil resources leads to several new problems. One of them is the high analytical effort to analyse a hydrolyzate completely for degradation products from cellulose, hemicellulose, lignin and pectin. Normally, several chromatographic techniques as well as UV-determination have to be used in order to determine the final sugar concentration as well as the concentration of potential inhibitors [1].
Thus, the aim of this study was to develop a method which allows for the simultaneous determination of all soluble products derived from cellulose, hemicellulose, lignin and pectin.
Consequently, the behavior of 25 model substrates from biomass in the HPAEC-PAD has been investigated as the HPAEC-PAD is the common way for the determination of soluble cellulose and hemicellulose products [2]. A method development with a varying eluent composition (100 mM NaOH, 200 mM NaOH, 100 mM NaOH/500 mM NaOAc and water) and column oven temperature (30, 40 and 50 °C) led to a separation of the desired sugar glucose and the potential inhibitors. The inhibitors could be determined up to a concentration as low as 22 mg/L and divided into the three groups 5-hydroxymethylfurfural, the glucose degradation product, and alcoholic as well as phenolic lignin products.
Consequently, this method was used to characterize 17 different hydrolyzates from various biomasses. The final concentrations of glucose varied from 0.024 g/L for beechwood xylan to 2.5 g/L for cellulose. However, the sum of the inhibitors varied from 0.022 g/L for water melon peel to 0.24 g/L for beechwood xylan.

References

[1] A. Sluiter, B. Hamas, R. Ruiz, C. Scarlata, J. Sluiter and D. Templeton, NREL/TP-510-42618, LAP (2008)
[2] A. Nagel, S. Sirisakulwat. R. Carle and S. Neidhart, Journal of Agricultural and Food Chemistry, 62, 9 (2014), 2037-2048

Application of analytical distillation tools for the sample production of lube base oil

A. George, M. Berthod, N. Chandak and M. Nasser Al Shebli

Takreer Research Centre, Abu Dhabi U.A.E

E-mail: ageorge@takreer.com

Separation techniques play a major role in the production of petroleum distillates in a refinery. Lube Base Oil production is of interest due to higher margins and availability of specific feed fractions within the refinery process streams. Heavy Vacuum Gas Oil (HVGO) hydrocracker bottoms called Unconverted Oil (UCO) are the best feed for the production of Base Oil. Production process involves selection of appropriate cuts / fractions of UCO to be processed in hydro dewaxing and hydro finishing reactors. Products from these processes are to be suitably fractioned again for the final Base oil grades of Group II & Group III with specific viscosity classification.

The research centre had to produce certain quantity of the base oil products prior to the commissioning of the base oil units at the refinery utilizing the Pilot plants and various analytical distillation tools of specific nature. GC Simulated distillation used for the identification of boiling range and yield patterns leading to the finalization of cut points in atmospheric column, True Boiling Point (TBP) & Hi Vacuum Pot still distillations and lab scale vacuum distillation units were also used to collect small quantity of fractions for finalization of feed and targeted product fractions meeting the required quality specifications.

Distillation Tools Used	Test Method Applied	Application in this project	Applicable Boiling Range (°C)	Capacity or Volume required
GC-Simulated Distillation	ASTM D 2887	Estimation of Hydrocracker Conversion, Yield Prediction and cut Point Finalization of Base Oil	55 -538	0.1µl of Neat / Diluted in CS_2
GC- High Temperature Simulated Distillation	ASTM D 7169	Boiling Range evaluation of HVGO, Residues & cut Point Finalization of Base Oil	55 – 720	0.1µl of Neat / Diluted in CS_2
Vacuum Distillation	ASTM D 1160	Boiling range evaluation and quality check	150 - 580	200 ml
True Boiling Point Distillation (6L Unit)	ASTM D 2892	Distillation of Hydrocracker effluent for yield & quality evaluation.	15 - 400	Up to 4 Ltrs.
True Boiling Point Distillation (200L Unit)	ASTM D 2892	Distillation of Hydrocracker effluent for UCO Production	15 - 400	Up to 150 Ltrs.
Hi Vacuum Pot still Distillation (50L Unit)	AST D 5236	Fractionation of UCO & Production of Base Oil	150 - 565	Up to 35 Ltrs.

Table -1: Distillation tools used and their application

This presentation will provide the detailed application of GC - Simulated Distillations, Vacuum Distillation; TBP & Pot still distillation and their fine-tuning of parameters in the sample production of Group II & Group III base oil products. Application of the laboratory scale and batch distillation could successfully support production of Group II, Group III base oil products meeting all the specifications.

Invited lecture

Membrane-based sample preparation techniques for chromatographic analysis

W. Frenzel

Technische Universität Berlin, Institut für Technischen Umweltschutz, Str. d. 17. Juni 135, D-10623 Berlin (Germany)

E-mail: wolfgang.frenzel@tu-berlin.de

IL15

Membrane-based sample preparation coupled to chromatographic separation is an area of research and development having found considerable interest within the scientific community. However, despite the many attractive features and opportunities offered by membrane-based sample preparation the transfer into routine applications has - in the opinion of the author -not yet appropriately taken place.

In the lecture a brief outline of different membrane separation techniques including dialysis, pervaporation and membrane extraction will be given and aspects of selectivity enhancement of the respective techniques discussed. Options of analyte preconcentration will also be presented. Various instrumental configurations of membrane separation modules and their implementation into flow-through systems will be presented and the benefits arising from direct coupling to chromatographic systems demonstrated.

The beneficial features of membrane based sample preparation become apparent in the analysis of complex environmental, clinical and industrial samples. In several applications at our department such kind of samples are routinely analysed circumventing (or at least dramatically simplifying) the common sample preparation necessities prior to sample injection. Comparison with conventional sample preparation procedures revealed the benefits of the developed procedures, including automation feasibility, low risk of contamination as well as high accuracy and precision.

A particular focus of the lecture will be set on microdialysis. This is a well proven in-vivo sampling technique for neurochemical and pharmacokinetic studies which has only more recently been exploited for environmental samples. Application to the monitoring of ionic contaminants in a variety of samples including interstitial water of sediments and soil is used to exemplify the unique potentialities of this method for environmental studies.

Wednesday 23 September 2015

Royal Cruise Hall-D

Chair: R. Lobinski, M. Karayannis

Chromatography 2

Incurred Sample Reanalysis: Considerations on the novel regulatory requirement in bioanalysis

Y. Dotsikas

Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Athens, Panepistimioupoli Zografou GR - 157 71, Athens, Greece

E-mail: idotsik@pharm.uoa.gr

Incurred sample reanalysis (ISR) is a recent requirement by regulatory agencies to demonstrate reliability of bioanalytical measurements [1,2]. In order to pass ISR, regulatory recommendations require that 67% of ISR (unknown) samples be within 20% of the average of original and reanalyzed values. A failed ISR requires an investigation to determine why the assay is not performing at the same level during sample analysis as compared to the initial method validation runs. On the other hand, a successful ISR assessment helps to improve confidence in the reliability of data.
Several recent publications have demonstrated that incurred sample reanalysis can reveal various methodological and/or operational issues that may lead to bioanalytical errors. These issues include, but are not limited to, instability of the analyte(s) of interest, suboptimal sample preparation procedures, population specific matrix effect and/or interference, inadvertent sample switching, inadequate chromatographic selectivity and sample nonhomogeneity.
Therefore, a consideration of the aforementioned issues along with potential solutions would be very helpful in modern bioanalytical methods.

References

[1] FDA, Guidance for Industry: Bioanalytical Method Validation (Draft guidance), *FDA*, 2013, Available at: http://www.fda.gov/downloads/Drugs/GuidanceComplianceRegulatoryInformation/Guidances/UCM368107.pdf

[2] European Medicines Agency, Guideline on Validation of Bioanalytical Methods, *European Medicines Agency*, 2009, Available at: http://www.ema.europa.eu/docs/enGB/documentlibrary/Scientificguideline/2011/08/WC500109686.pdf

3 Years of Stirring-Assisted Lab-In-Syringe: Development, Applications, and Potentials

B. Horstkotte, P. Solich

[1]Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové, Charles University in Prague, Heyrovského 1203, Czech Republic

E-mail: Horstkob@faf.cuni.cz

WE06

A glass syringe is simultaneously a sealed yet size-adaptable compartment enclosed by a transparent and chemically inert material. It can therefore be used for solution measuring, mixing, and propulsion, as well as a detection cell.
In 2012, the idea of using the void of a syringe of a computer controlled syringe pump as reaction vessel to automate liquid-liquid microextraction (LLME) had led to the technique Lab-In-Syringe (LIS) [1] with ca. 20 publications up-to-date.
The analyzer system follows the design of nowadays well-established flow technique Sequential Injection Analysis (SIA) [2] with basic components being a selection valve, a syringe pump, and a detector. While SIA is mostly used to automate and miniaturize SPE procedures, LIS is ideally suited to automate LLME protocols.
Computer-controlled choice of parameters, simplicity of instrumentation, and versatility of operation are the main features of LIS being promoted by using a magnetic stirring bar inside the syringe [3]. Creation of a rotating magnetic field forces the stirring bar to rotate, which enables in-syringe homogenous and reproducible mixing of all aspirated solutions as well as efficient dispersion of immiscible phases. Procedures based on the mixture of large volumes of solutions with different viscosities (difficult to automate with most flow techniques) become straightforward with LIS. Moreover, direct transfer of standard protocols to LIS is possible and predictable.
In this presentation, a synopsis of the different approaches, selected applications, and a brief outlook and discussion about the potential of LIS will be given.

B.H. was supported by Charles University Research Centre (UNCE 204026/2012). The work was co-financed by the European Social Fund and the state budget of the Czech Republic (project TEAB CZ.1.07/2.3.00/20.0235).

References

[1] F. Maya, B. Horstkotte, J.M. Estela and V. Cerdà, *Anal. Bioanal. Chem.* 404 (2012) 909-917.
[2] J. Růžička and G.D. Marshall, *Anal. Chim. Acta* 237 (1990) 329-343.
[3] B. Horstkotte, R. Suárez, P. Solich and V. Cerdà, *Anal. Chim. Acta*, 788 (2013) 52-60.

Fast method for the determination of residual solvents in radiopharmaceutical products

M. Mihon[1,2], C. Tuta[2], A.C. Ion[1], D. Niculae[2] and V. Lavric[1]

[1]University Politehnica of Bucharest, 313 Splaiul Independentei St., Bucharest, Romania
[2]National Institute for Physics and Nuclear Engineering "Horia Hulubei", 30 Reactorului St., Magurele Ilfov, Romania

E-mail: mirela.mihon@nipne.ro

The aim of this work was the developing and validation of a fast analytical method to determine the residual solvents content in radiopharmaceuticals such as: ^{18}F-FDG, ^{18}F-FES, ^{18}F-NaF, ^{18}F-FAZA.

Radiopharmaceuticals are radioactive preparations for medical purposes used in nuclear medicine as tracers in diagnostic imaging and treatment of certain diseases. Positron Emission Tomography (PET) is a medical imaging technique that consists in introducing into the body of a small amount of a biologically active chemical compound labelled with a short lived positron-emitting radioisotope (^{18}F, ^{11}C, ^{68}Ga).

Residual solvents are critical impurities in radiopharmaceuticals that can affect labelling and physicochemical properties of drugs. Therefore, the determination of these solvents is essential for quality control of radiopharmaceuticals. Validation of the control method for residual solvents by gas chromatography is referred by the European Pharmacopoeia [1] using a special injection technique (head space)[2]. Gas chromatography has excellent selectivity and good sensitivity with flame ionization detection (FID), therefore, the proposed method is reducing the time needed for determination of ethanol, acetone, and acetonitrile.

The parameters of the method, which comply with International Conference on Harmonization guideline and regulation, are: accuracy, precision, linearity, limit of detection, limit of quantification and robustness [3]. ICH guideline Q3C lists acetone and ethanol as a Class 3 solvents and their presence in radiopharmaceuticals may be regarded as being of low risk to human health. The solvents should be considered separate from stabilizers, which is usually added to in radiopharmaceutical preparation in significant concentrations 5% and 12% [4,5].

The proposed method (direct gas chromatography injection) proved to be linear, precise, accurate and robust. Good linearity was achieved for all the solvents and correlation coefficients (R^2) for each residual solvent were found more than 0.99.

Acknowledgments

"This work is supported by the Sectorial Operational Program Human Resources Development (SOP HRD), financed by the European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390/"

References

[1] European Pharmacopoeia, 8.0 Edition (2014)
[2] Mihon et al., *Environmental Engineering and Management Journal*,14 (2015) 289-296
[3] ICH Guidelines, Impurities: Guideline for residual solvents Q3C(R5), Feb 2011
[4] R. P. Klok, A.D. Winhorst, *Nuclear Medicine and Biology*, 33 (2006) 935-938
[5] M.S.Jacobson et al., *Applied Radiation and Isotopes*, 67 (2009) 990-995

Different approaches to determination of acid dissociation constants of warfarin and hydroxywarfarins using capillary electrophoresis

M. Woźniakiewicz[1], P. Nowak[1], M. Mitoraj[2], P. Olechowska[1] and P. Kościelniak[1]

[1]Department of Analytical Chemistry, Faculty of Chemistry, Jagiellonian University in Kraków, Ingardena 3, 30-060 Kraków, Poland
[2]Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University in Kraków, Ingardena 3, 30-060 Kraków, Poland

E-mail: michal.wozniakiewicz@uj.edu.pl

Warfarin (WAR) is a widely prescribed drug exhibiting anticoagulant activity, used in the prevention of thrombosis and thromboembolism, i.e. formation of blood clots and vascular occlusions. WAR is also characterized by the complex, region- and enantioselective oxidative metabolism, conducted by several different forms of cytochrome P450. The main phase I metabolites of WAR are hydroxywarfarins: 3'-hydroxywarfarin, 4'-hydroxywarfarin, 6-hydroxywarfarin, 7 hydroxywarfarin, 8-hydroxywarfarin and 10-hydroxywarfarin. The therapeutic activity of WAR is dependent on its ionization level and for that reason, the acid dissociation constant (p*K*a) of WAR is important from the pharmacological point of view [1,2]. Another issue is the acid-base properties of hydroxywarfarins, till now, not fully recognized. In contrary to the parent drug, they are supposed to be capable of a double dissociation, which makes the prediction of their ionization-related properties more complex. Therefore, experimental determination of their accurate pK_{a_1} and pK_{a_2} values is undeniably desirable for pharmacokinetic studies.

In the present study different approaches to determination of p*K*a using the capillary electrophoresis technique have been investigated. The capillary zone electrophoresis (CZE) method, based on the relation between effective electrophoretic mobilities and pH has been found as an efficient and accurate tool, while the spectrophotometric method (CZE-DAD) and the internal standard method (IS-CZE) have been assessed as promising alternative approaches. The CZE-DAD method based on the change in the shape of absorbance spectra between acidic and basic forms is a combination between capillary electrophoresis and spectrophotometric titration, and it has yielded very consistent values of pK_{a_1} (first dissociation) with those obtained by CZE. The IS-CZE method in turn, has enabled the estimation of pK_{a_1} and pK_{a_2} within only two analytical runs, however results have been less accurate than in the case of CZE and CZE-DAD. Finally, the Debye-Hückel model has been used for determination of thermodynamic pK_{a_1} and pK_{a_2} of hydroxywarfarins, referring to the zero ionic strength.

References

[1] H. Wan, A. Holmen, M. Någård and W. Lindberg, *J. Chromatogr. A*, 979 (2002) 369-377.
[2] P. Nowak, M. Garnysz, M.P. Mitoraj, F. Sagan, M. Woźniakiewicz and P. Kościelniak, *J. Chromatogr. A*, 1377 (2015) 106-113.

Wednesday 23 September 2015

Royal Cruise Hall-A

Chair: G. Hieftje, F. Adams, A. Koliadima

Materials Science/ Spectroscopy 2

Invited lecture

Materials characterization at the nanoscale by X-ray spectrometry

B. Beckhoff, P. Hönicke, I. Holfelder, J. Lubeck, M. Müller, A. Nutsch, B. Pollakowski, C. Streeck, R. Unterumsberger and J. Weser

Physikalisch-Technische Bundesanstalt (PTB), Abbestraße 2-12, 10587 Berlin, Germany

The development of efficient nanoscaled materials requires the correlation of the materials' functionality with their chemical and physical properties. To probe these properties, analytical methods that are both sensitive and selective at the nanoscale are required. The reliability of most analytical methods is based on the availability of reference materials or calibration samples, the spatial elemental composition of which is as similar as possible to the matrix of the specimens of interest. However, there is a drastic lack of reference materials at the nanoscale. PTB addresses this challenge by means of a bottom-up X-ray analytical method where all instrumental and experimental parameters are determined with known contributions to the uncertainty of the analytical results. This first-principle based approach does not require any reference materials but a complete characterization of the analytical instruments' characteristics and, in addition, of the X-ray fundamental parameters related to the elements composing the sample. X-ray spectrometric methods allow for the variation of the analytical sensitivity, selectivity, and information depth needed to effectively reveal the spatial, elemental, and chemical specimen parameters of interest. Examples of interfacial speciation, elemental depth profiling, as well as layer composition and thickness characterizations in various nanoscaled materials will be given. Recent instrumental achievements provide access to liquid-solid interfaces as well as towards the in-situ speciation of nanocaled battery materials.

[1] R. Unterumsberger, B. Pollakowski, M. Müller, and B. Beckhoff, Anal. Chem. **83** (2011) 8623

[2] R. Unterumsberger, M. Müller, B. Beckhoff, P. Hönicke, B. Pollakowski, and S. Bjeoumikhova, Spectrochim. Acta B **78** (2012) 37

[3] F. Reinhardt, J. Osán, S. Török, A.E. Pap, M. Kolbe, and B. Beckhoff, J. Anal. At. Spectrom. **27** (2012) 248

[4] A. Delabie, S. Sioncke, J. Rip, S. van Elshocht, G. Pourtois, M. Müller, B. Beckhoff, and K. Pierloot, J. Vac. Sci. Technol. **A30** (2012), 01A127

[5] B. Pollakowski, P. Hoffmann, M. Kosinova, O. Baake, V. Trunova, R. Unterumsberger, W. Ensinger, and B. Beckhoff, Anal. Chem. **85** (2013) 193

[6] C. Becker, M. Pagels, C. Zachaus, B. Pollakowski, B. Beckhoff, B. Kanngießer, and B. Rech, J. Appl. Phys. **113** (2013) 044519

[7] C. Streeck, S. Brunken, M. Gerlach, C. Herzog, P. Hönicke, C.A. Kaufmann, J. Lubeck, B. Pollakowski, R. Unterumsberger, A. Weber, B. Beckhoff, B. Kanngießer, H.-W. Schock and R. Mainz, Appl. Phys. Lett. **103** (2013) 113904

[8] J. Lubeck, B. Beckhoff, R. Fliegauf, I. Holfelder, M. Müller, B. Pollakowski, F. Reinhardt and J. Weser, Rev. Sci. Instrum. **84** (2013) 045106

[9] I. Holfelder, B. Beckhoff, R. Fliegauf, P. Hönicke, A. Nutsch, P. Petrik, G. Roeder and J. Weser, J. Anal. At. Spectrom. **28** (2013) 549

[10] P. Hönicke, M. Kolbe, M. Müller, M. Mantler, M. Krämer, and B. Beckhoff, Phys. Rev. Lett. **113** (2014) 163001

[11] M. Müller, S. Choudhury, K. Gruber, V.B. Cruz, B. Fuchsbichler, T. Jacob, St. Koller, M. Stamm, L. Ionov, and B. Beckhoff, Spectrochim. Acta B **94-95** (2014) 22

Optimizing biosensors labels components and their discrimination efficiency using SEIRA methodology

A. Hornemann[1], D. Eichert[2], S. Flemig[3], G. Ulm[1] and B. Beckhoff[1]

[1] Physikalisch-Technische Bundesanstalt, Abbestrasse 2-12, 10587 Berlin, Germany
[2] Elettra – Sincrotrone Trieste, S.S. 14 Area Science Park, 34149 Basovizza, Trieste, Italy
[3] BAM Bundesanstalt für Materialforschung und -prüfung, Richard-Willstätter- Strasse 10, 12489 Berlin, Germany

E-mail: diane.eichert@elettra.eu

WE09

The need for technological progress in bio-diagnostic assays of high complexity requires both fundamental research and constructing efforts on nano-scaled assay recognition elements that can provide unique selectivity and design-enhanced sensitivity features for reliable high-performance analysis. Indeed, high-throughput capabilities require the simultaneous detection of various analytes combined with appropriate bioassay components. To design bioassays that function as molecular probes, a selective binding event has to be optimized with respect to the over whole physicochemical properties which may influence the successful readout of signals. This constitutes the core of the first design steps to elaborate multi-purposes bioassay platforms.

Nanoparticle induced sensitivity enhancement, and its related application to multiplexed capability Surface-Enhanced InfraRed Absorption (SEIRA) assay formats are fitting well these purposes. SEIRA constitutes an ideal platform to isolate vibrational spectroscopic signatures of bioassay' targeted and active molecules (as antibodies). Accordingly, the potential of diverse targeted bio-labels, here fluorophore-labeled antibody conjugates, chemisorbed onto low-cost biocompatible gold nano-aggregates SEIRA substrates has been explored for their use in assay platforms. Extensive areas of dried sample films were analyzed by synchrotron radiation FTIR/SEIRA spectro-microscopy and the resulting complex hyperspectral datasets, containing molecular SEIRA fingerprints, were submitted to automated statistical analysis, namely principal components analysis. Relationships and dependencies between chemical functional groups of the various antibody-fluorophore conjugation systems were determined for revealing their spectral discrimination capabilities.

These studies illustrate the potentiality of SEIRA methodology to select, optimize and qualify bio-label molecules, but what is more to evaluate, adjust and increase the efficiency of the substrates for ultimately screening in biological environment too.

Consequently, we demonstrate that robust spectral encoding via SEIRA fingerprints opens up new opportunities for a fast, reliable, enhanced and multiplexed high-end screening not only in bio-diagnostics but also in in vitro biochemical imaging.

References

[1] A Hornemann, D. Eichert, S. Flemig, G. Ulm and B. Beckhoff, *Physical Chemistry Chemical Physics*, 17 (2015) 9471-9479, doi:10.1039/C4CP05944A10.10.

Surface functionalization of sol-gel grown NiO thin films by Palladium nanoparticles for Hydrogen gas sensing

I. Sta[1], M. Jlassi[1], M. Kandyla[3], M. Hajji[1,2], P. Koralli[3] , M. Kompitsas[3] and H. Ezzaouia[1].

[1] Laboratoire de Photovoltaïque, Centre de Recherche et des Technologies de l'Energie, Technopole de Borj-Cédria, BP 95, 2050 Hammam-Lif, Tunisia
[2] Ecole Nationale d'Electronique et des Communications de Sfax, Technopôle de Sfax, Route de Tunis Km 10, Cité El Ons, B.P. 1163,*3021* Sfax, Tunisia
[3] National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, 48 Vasileos Konstantinou Ave., 11635 Athens, Greece

E-mail: mcomp@eie.gr

Palladium (Pd) nanoparticles were used to partially cover via pulsed laser deposition (PLD) the surface of nickel oxide (NiO) thin films that had been prepared by the sol–gel method on glass substrates. The structural and morphological properties of these NiO:Pd films were studied using X-ray Diffraction, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). It was found that the films crystallized in cubic NiO crystalline structure. SEM observations showed that the metallic nanoparticle dimensions and geometry depends on the Pd deposition time, while NiO films surface remains nano-structured, granular and very smooth. The optical properties of the films were studied using UV–visible spectroscopy. As grown NiO and NiO:Pd compound thin films were tested as hydrogen sensors. The response of NiO and NiO:Pd (for 1min and 2min deposition time) thin films against hydrogen was investigated at different operating temperatures and for various gas concentrations. The addition of metallic nanoparticles was found to decrease the detection limit, the operating temperature (from 180 °C to 56 °C) and the response time of the sensors, while increasing the sensing response signal by a factor of 20. A correlation of the nanoparticles concentration with the optimum operating temperature was found that may lead to hydrogen selectivity in sensor arrays.

Hydration Study of Oil Well Cements and the relation with their Chemical and Physical Characteristics

D. Velissariou[1], N. Katsiotis[1], P. Tsakiridis[2], M. Beazi-Katsioti[1]

[1]School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou St., 157 80 Athens, Greece
[2]School of Mining & Metallurgical Engineering, National Technical University of Athens, 9 Heroon Polytechniou St., 157 80 Athens, Greece

E-mail: katsioti@central.ntua.gr

WE11

In order to explore for petroleum resources, drilling has to happen to deeper depths where the temperature and pressure, are elevated. The ordinary construction materials cannot assure tolerance in such High Pressure/High Temperature (HPHT) conditions and possible failures during the oil well construction can cause important social, environmental and economic impacts. Strict standards, created by the American Petroleum Institute (API) and adopted by the International Organization of Standardization (ISO), define the requirements for the materials used during the whole Oil-Well Construction Procedure. Specifically, Oil-Well Cements' (OWC) Chemical and Physical Requirements are described in API 10A, 24th Edition/ISO 10426-1:2009 - Specification for Cements and Materials for Well Cementing. A classification procedure follows based on the results of the required tests. The classes of OWC are A, B, C, D, E, F, G, H and the most common used for cementing deep oil-wells are G and H classes. At the present study two Oil Well Cements Class G are examined, one commercially available and the other laboratory-produced. These cements were examined with X-ray fluorescence (XRF) analysis and thickening time, compressive strength and free fluid test were performed to the cement slurries, to verify that both of them meet the standard requirements. The hydration of OWC can be radically different than the ordinary Portland cements because of the elevated pressure and temperature of the deep oil wells. Also due to the restrictions to the composition of OWC according to the standard and the differences between the two cements, they are studied for their hydration process. The two cement slurries are prepared according to the API 10A procedure and they are cured for 2, 7, 28 and 90 days in ambient condition. X-ray diffraction and TG/DTG analyses were used for the determination of the hydration products.

Synthesis and characterization of Paramagnetic Fe_3O_4 nanoparticles @ graphene oxide nanohybrid material

D. Karampatsos[1], A. Ntziouni[1], G. Efthymiou[1], K. Fujisawa[2], M. Terrones[2,3] and K. Kordatos[1]

[1]School of Chemical Engineering, Laboratory of Inorganic & Analytical Chemistry, National Technical University of Athens, 9 Iroon Polytechniou Str., Zografou Campus, Athens 15 780, Greece
[2]Department of Physics and Center for 2-Dimensional and Layered Materials, Pennsylvania State University, University Park, PA 16802, USA
[3]Department of Chemistry, Department of Materials Science and Engineering and Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA

E-mail: kordatos@central.ntua.gr

Magnetic graphene oxide (GO) nanohybrids were synthesized via the self-assembly method. GO was prepared by modified Hummers method, which involves the oxidation of graphite to produce graphite oxide, which in turn was exfoliated by means of ultrasonic treatment to form GO. The GO platform was functionalised with surfactants Cetyl trimethylammonium bromide (CTAB) and poly (sodium 4-styrenesulfonate) (PSS) and then was dispersed in ethylene glycol (EG). Magnetic nanoparticles (NPs) were formed by an in situ conversion of $FeCl_3$ to Fe_3O_4 via a solvothermal treatment. The final hybrid materials were formed on the basis of electrostatic attraction. First, positively charged CTAB molecules anchored to the surface of GO as a result of electrostatic forces, and then the anionic polyelectrolyte PSS was absorbed to form a solid polymer layer on the nanosheets. Due to the high density of the sulfonic groups within the negatively charged polyelectrolyte PSS, Fe^{3+} ions in solution would interact with the sulfonic groups by electrostatic attraction, then these ions partially reduced to Fe^{2+} ions and subsequently co-precipitate as Fe_3O_4 NPs during the solvothermal treatment. As a result, the NPs loading process depends on the functionalisation of GO. The positive metal ions can be adsorbed preferably at some sites due to imperfections of GO sheets, which serve as the nucleation sites for the formation of larger crystals.
The attachment of Fe_3O_4 NPs on GO was confirmed by X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscopy (HRTEM), Thermogravimetric Analysis (TGA), Raman Spectroscopy and SQUID (Superconducting Quantum Interference Device) Magnetometer. NPs exhibited good crystallinity, nanoscale size and uniform distribution, size and morphology, whilst the GO nanosheets showed minimum agglomerations. The final materials demonstrated good thermal stability and superparamagnetic behavior.

References

[1] Yong Liu, Wei Jiang, Song Li, Fengsheng Li, Applied Surface Science 255, (2009) 7999–8002
[2] Yixuan Zhang, Yuxiao Cheng, Ningning Chen, Yuyan Zhou, Bingyu Li, Wei Guet al., Journal of Colloid and Interface Science 421 , (2014) 85–92
[3] Guangshuo Wang, Guangyi Chen, Zhiyong Wei, Xufeng Dong, Min Qi, Materials Chemistry and Physics 141, (2013) 997-1004
[4] Ferrari A. C., Meyer J. C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F. et al., Phys. Rev. Lett. 97, (2006) 187401-1-4

Invited lecture

Atomic Fluorescence Spectroscopy – Analytical Curiosity or Useful Tool

L. Ebdon

University of Bedfordshire, Park Square, Luton, Bedfordshire, LU1 3JU, United Kingdom

E-mail: Les.Ebdon@beds.ac.uk

IL17

In 1962, Alkemade first suggested that the re-emission of radiation from radiatively excited atoms, termed atomic fluorescence spectroscopy (AFS) could be analytically useful. In the late 1960s and 1970s the research groups of Winefordner in the USA and West in Europe published extensively on analytical applications of AFS, yet the technique has never enjoyed the popularity of atomic absorption spectroscopy, plasma generated atomic emission spectroscopy or atomic mass spectrometry. This lecture will explore this phenomenon and detail some niche analytical areas where AFS is still seen as a useful tool in an analyst's armoury.

The basic technique of AFS, including the 6 types of fluorescence commonly observed, will be described together with the instrumentation needed for practical measurements. Particular attention will be given to radiation sources and suitable atom cells. It will be shown how the search for highly intense but stable light sources held back AFS at a critical time. It will also be shown how the preference for cool atom cells using low collisional cross section fuels has led to the present niche applications of AFS.

Cold vapour and hydride generation techniques seem ideally suited to AFS, the reasons for this will be explained and several modern applications of the technique described. Examples of the use of AFS to measure mercury, arsenic and selenium in environmental and food samples will be given as well as examples of the use of the technique to aid in the determination of the speciation of these elements in real samples.

The lecture will be illustrated by a variety of applications and the author's nearly 50 years involvement with AFS, an elegant but elusive analytical technique.

Wednesday 23 September 2015

Royal Cruise Hall-A

Chair: B. Beckhoff, K. Ochsenkühn

Archaeometry

Invited lecture

Tales of Archaeometry from Anatolia

O. Y. Ataman[1], Ü. Muşkara[2] and M. Aydın[3]

[1]Department of Chemistry, Middle East Technical University, 06800 Ankara, Turkey
[2]Kocaeli University, Department of Conservation and Restoration, 41380 Kocaeli, Turkey
[3]Batman University, Department of Archaeology, 72100 Batman, Turkey

E-mail: ataman@metu.edu.tr

Two cases of archaeometric research will be presented. The first one is related to the origin of raw material for the dolomite figurines found in Emecik, Turkey. There are studies showing that the raw material for these figurines found in West Anatolia were brought from Cyprus [1]. The present study has shown that for some figurines, the raw material is likely to be originated from the local sources. For this provenance study, determinations of Mg, Fe, Ba, Sr, Mn were done using ICP-OES; while ICP-MS was used for Cr, Y, Nb, Hf, La, Ce, Nd, Sm, Eu, Gd, Ho, Er, Yb and Lu contents. In addition, thin section analysis and XRD patterns were also used.

The second case is related to the authentication of some silver Roman coins employing portable XRF which has been in use for archaeometry for almost last two decades [2]. Problems of accuracy and precision exist in this technique. Nevertheless, as long as the analytical results to be compared are too different from each other, useful results can be obtained. In this case the key elements were Ag, Cu, Zr, Pt, Pb and Bi. Approaches to deal with repeatability issue will be discussed.

As concluding remarks, the case of artefacts stolen from musea will be discussed and the feasibility of archiving the results of non-destructive techniques for the museum subjects will be discussed.

References

[1] K. Polikreti, Y. Maniatis, Y. Bassiakos, N. Kourou, V. Karageorghis, *J. Archaeol. Sci.*, 31 (2004) 1015-1028.
[2] A. Longoni, C. Fiorini, P. Leutenegger, S. Sciuti, G. Fronterotta, L. Strüder, P. Lechner, *Nucl. Instrum. Methods Phys. Res., Sect. A*, 409 (1998) 407-409.

Invited lecture

Contribution of analytical chemistry in environmental and cultural physical sciences

J. A. Stratis, Hussein Hasa M.H. Mahmoud , C. Makarona, E. Daftsis, N. Kantiranis, El. Charalampous, A.C. Charalambous, D.N. Papadopoulou, A.M.A. Mousa, N. Tsirliganis

Aristotle University, 54124 Thessaloniki, Greece

e-mail: jstratis@chem.auth.gr

Environmental and Cultural Sciences are connected strongly with our life. Thus, UNEP adapted one emblem for Environmental and Cultural HeritageProtection. The combination of Applied Analytical with other scientific fields, such as Applied Mineralogy creates excellent tools for the optimum service to both ofthem.

The study, analysis and recording of materials of which our cultural heritage is built, and the changes that it has undergone over the centuries from the effect of environmental and
Anthropogenic factors, as well as, the investigation of the mechanisms of deterioration anddegradation of monuments, can be explained by the contribution of analytical chemistry combined with applied mineralogy and applied mathematics. The composition of construction materials, characterizationof weathering products and the investigation of the deterioration mechanisms are the key pillarsin the study and protection of cultural heritage. Some examples of our work, dealingwith Cultural heritage studies and Environmental protection studies are given.

References

1. “Application of Atomic Absorption Spectrometry in the study of ancient Glassmaking” E. A. Mirtsou, Ph.D. Thesis, Aristotle University, Thessaloniki 2000
2. “Development and accreditation of multielemental analytical methods (ICP-AES and m-XRF).Application to the ancient Abdera (Thrace, Greece) ceramic.” D.N. Papadopoulou Ph.D. Thesis, Aristotle University, Thessaloniki 2005
3. “Assessing the Decay Agents of Wall Paintings in Al Quarna and Wadi El Natrun Regions – Egypt”, Abu Bakr M.A. Moussa Ph.D. Thesis, Aristotle University, Thessaloniki 2007
4. “Study of the chromatic changes of the Ancient Pigments in some wall paintings in Egypt and the Procedures of Conservation”, Hussein Hasa M.H. Mahmoud Ph.D. Thesis, Aristotle University, Thessaloniki 2009
5. “Research of the manufacturing technology and identification of the Cyprus workshops floor Mosaics 2nd-7th century .AC. with chemical and Physical Chemical methods” El. Charalampous, Ph.D. Thesis, Aristotle University, Thessaloniki 2009
6. “Study of Byzantine Cypriot Glazed Pottery. Investigation of Manufacture Technology and Provenance with Physicochemical methods”, A. Charalampous, Ph.D. Thesis, Aristotle University, Thessaloniki 2010
7. Sustainable Management of mine wastes, case study: The old Olympias mixed Sulphides Tailing. E. Gazea, E. Daftsis, N. Papafilipou, J. Stratis, D. Alifragis, 3rd International Conferenceon Industrial and Hazardous Waste Management, Crete 2012

Invited lecture

The use of instrumental analysis for investigations in archeology and history of arts: some cases with exceptional interest for the society

M.I. Karayannis

University of Ioannina, Department of Chemistry

E-Mail: mkaragia@cc.uoi.gr

IL20

Instrumental Analysis occupies a leading role in the investigation of questions of Archaeology or History of Fine Arts, in cases of erroneous or dubious conclusions appearing in studies in these scientific areas. Natural sciences are called in to reconcile controversial results between different Archaeologists and Fine Art Historians.
In this presentation we will present and describe specific cases and we will refer to instrumental analytical approaches which were applied in order to answer critical questions. Among such cases which are of interest we will refer to:

1) The "***Turin Shroud or Holy Shroud***", which was studied by *Accelerator Radiocarbon Dating.*

2) The case of the forgeries of the fateful Dutch painter **Han Van Meegeren,** who forged the paintings of the 17-century Dutch artist Vermeer: The case was investigated by measuring *Natural Alpha Emitters*.

3) The case of the painting **"*La Bella Principessa*"** of Leonardo Da Vinci: In this case, archaeometrists were able to identify faint fingerprints on the canvas using *Infrared Reflectometry and Radiocarbon Dating*.

4) The cases of the paintings "***Virgin and Child with Saints***" of **Pietro Perugino** and "***The Landscape Drawings"*** of **Peter Brügel**, were investigated applying ***Statistical Analysis of Digital Images and the Wavelet Decomposition Method.***

Wednesday 23 September 2015

Royal Cruise Hall-B

Chair: K. Kordatos, D. Eichert, F. Tsopelas, L. Tsakanika

Poster Session 3

Materials Science

Electrochemistry

Environmental analysis

Graphene oxide-based sensing system for detection of double-stranded DNA

A. Giannakopoulos[1], I.K. Kyriakou[1], D. Tasis[2,3], D.P. Kalogianni[1], K. Papagelis[2,4], P.C. Ioannou[5], and T.K. Christopoulos[1,2]

[1]Department of Chemistry – University of Patras
[2]Fdn Res & Technol Hellas, Inst Chem Engn Sci, GR-26504 Patras, Greece
[3]University of Ioannina, Department of Chemistry, 45110 Ioannina
[4]University of Patras, Department of Material Science, Patras 26504, Greece
[5]Department of Chemistry – National and Kapodistrian University of Athens

E-mail: tchrist@upatras.gr

Nanomaterials and nanostructures, including metal-, silica- and carbon-based nanoparticles, carbon nanotubes, quantum dots, and graphene oxide, offer fascinating opportunities for the development of novel sensing systems due to their unique physical, chemical, mechanical, electrical, magnetic and optical properties. Graphene oxide (GO), a single atom thick two-dimensional carbon nanomaterial, has been proven to possess many unique properties, including high affinity for single-stranded DNA (ssDNA), through π–π stacking interaction, as well as efficient quenching of photoluminescence based on either energy transfer or electron transfer mechanism. These properties provide a great opportunity for the fabrication of graphene-based DNA methods and sensors. GO has been used for the development of sensors for the detection of small molecules, metal ions, nucleic acids and proteins. In this work, the detection of specific dsDNA sequences based on hybridization and graphene oxide has been accomplished. The oxygenated form of graphene was prepared by adopting a two-step protocol, involving oxidation of graphite flakes, as described in our recent study [1]. A dye-labeled specific oligonucleotide-probe (ssDNA) was used as reporter for the identification of the corresponding dsDNA sequence. More specifically, heat denatured dsDNA sequence was initially hybridized to complementary fluorescein-labeled oligonucleotide probe and the hybrid was treated with exonuclease III. This enzyme specifically catalyzes the removal of mononucleotides from the blunt 3' termini of dsDNA. Exonuclease III is not active on single-stranded DNA, and thus 3´-protruding termini are resistant to cleavage. An increase in the fluorescence intensity is observed after the addition of GO to the solution, when dsDNA target has been formed. In the absence of dsDNA target, the fluorescein-labeled oligonucleotide-probe is absorbed from GO via π-π interaction, resulting to efficient fluorescence quenching due to energy transfer mechanism.

References

[1]. A. Nikolakopoulou, D. Tasis, L. Sygellou, V. Dracopoulos, C. Galiotis, P. Lianos, *Electrochimica Acta*, 111 (2013) 698-706.

Formation of graphene nanosheets from graphene oxide thin films via one-step heat treatment

D. Karampatsos, A. Ntziouni, G. Efthymiou and K. Kordatos

Laboratory of Inorganic & Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Str., Zografou Campus, Athens 15 780, Greece
E-mail: kordatos@central.ntua.gr

P3-02

A facile way to produce Graphene nanosheets (GNR) with very low concentration of oxygen functional groups is the reduction and exfoliation of thin Graphene Oxide (GO) films, which are formed by cleavage of graphite oxide (GTO) [1]. In our work, GTO was prepared from graphite powder via an oxidation protocol and GO by cleavage of the product with sonication [2]. GO films were transformed to GNR via a thermal annealing reduction process. GO was placed in a quartz tube in vacuum and was heated rapidly by a torch along the entire length. Shortly, expansion and exfoliation of GO occurred, due to formation of CO, CO_2 gases, a phenomenon indicative of the simultaneous decomposition of oxygenated groups.

In XRD analysis, graphite shows a sharp (002) peak of at $2\theta = 26.92^{o}$, whilst GO films exhibit a (001) peak at $2\theta = 10.98^{o}$ with bigger interlayer spacing, depicting the retention of the AB stacking [3]. GNR show no prominent peak, indicating the full exfoliation down to few-layer structure. FTIR spectra of GO consists of characteristic peaks of oxygenated groups, confirming the oxidation of graphite. Regarding GNR, the peaks of the functional groups almost disappear, whilst the weak peak at 672 cm^{-1} is owed to vibrations of C-C bonds that come up as defects due to thermal annealing. FESEM images reveal the sheet-like, stacked morphology of GO films [Fig.1(a)]. The single-layer structure features of GNR become visible after the thermal process, with a layered structure of minimum thickness and smooth surface being observed [Fig. 1(b)] [4]. TGA/DTA analysis evinces the expected greater thermal stability of GNR, due to the former thermal treatment. Raman spectra of GO evicts the D peak, in addition to the G, 2D peaks of graphitic structure, as a result of the defects imposed by oxidation. GNR Raman spectra differs mainly on the shape and position of 2D peak, which is close to that of bilayer graphene. Finally, I_D/I_G intensity ratio slightly increases for GNR, due to lattice defects caused by thermal annealing [5].

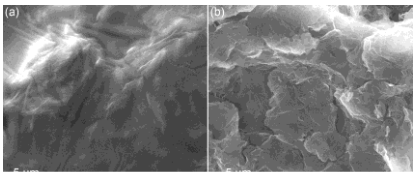


Fig. 1-FESEM images of GO (a) and GNR (b)

The above results suggest that one-step heat treatment is a simple route for graphene-like materials production, with good structural properties and few defects.

References

[1] Songfeng Pei, Hui-Ming Cheng, Carbon, 50 (2012) 3210–28
[2] Minas M. Stylianakis, George D. Spyropoulos, Emmanuel Stratakis, Emmanuel Kymakis, Carbon, 50 (2012) 5554–61
[3] Yixuan Zhang, Yuxiao Cheng, Ningning Chen, Yuyan Zhou, Bingyu Li, Wei Gu et al., Journal of Colloid and Interface Science, 421 (2014) 85–92
[4] Yu Li, Guodong Sheng, Jiang Sheng, Journal of Molecular Liquids, 199 (2014) 474-80
[5] O. Akhavan, Carbon, 48 (2010) 509–519

Selective fractionation of crude oil by means of separation techniques for analytical and preparative applications – a case of asphaltenes

M. Momotko, D. Chruszczyk, P. Makoś, G. Boczkaj

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P3-03

Asphaltenes are a group of components characterized by their physico-chemical properties, usually named as a fraction insoluble in straight chain aliphatic hydrocarbons. They are a natural component of crude oil. For the sake of the ability to uncontrolled precipitation from crude oil and formation of emulsions, asphaltenes state a big challenge for refinery and petrochemical industry. They can form deposition on the valves and other components of the pipeline. From this reasons the deasphalting process is very important. Asphaltenes are also an important fraction of residuum from vacuum distillation of crude oil. In this case their presence is valuable for production of bitumen. To increase the content of asphalthene fraction, raw vacuum residuum is oxidized, to obtain high quality material having even 30-40% mass of asphaltenes.

This paper presents a summary of the asphaltenes isolation techniques from crude oil, atmospheric and vacuum distillation residues as well as bitumens. Methods based on: selected precipitating solvent (or their mixtures), proportion to the used materials, temperature and contact time are summarized. The paper describes an examples of studies about PTV chambers tests based on the pressure and temperature change. Methods for the purification and further fractionation of the precipitated asphaltenes are described in details. Analysis of the results revealed a strong correlation between the physicochemical properties of the tested fractions, isolation techniques and raw material used in the study. On their basis it can be said that the percentage amount of precipitated asphaltenes decreases with increasing number of carbon atoms in the solvent used and with their molecular weight while the efficiency increases with the increase of material to solvent ratio. These and other detected dependencies allows to model the process parameters to obtain a fraction having strictly planned properties and maximize the efficiency of its isolation.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Center for Research and Development, Warsaw, Poland – Project LIDER, no. LIDER/036/573/L-5/13/NCBR/2014.

Determination of thiocyanate and other inorganic ions in placenta samples

S. Narkowicz[1], Ż. Polkowska[1], B. Kiełbratowska[2], J. Namieśnik[1]

1-Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, Gdańsk, Poland, phone: +48 58 347-21-10, fax: +48 58 347-26-94, 2-Department of Obstetrics, Medical University of Gdańsk, Gdańsk, Poland
3-Chair of Analytical Chemistry, Faculty of Chemistry, University of Sofia, Bulgaria

E-mail: sylwianarkowicz@10g.pl

P3-04

A special case of exposure to substances present in tobacco smoke, in an active or passive manner, is the exposure of a pregnant woman during pregnancy or a breastfeeding woman. As a result of that exposure, toxic compounds get into a woman's organism and can have a negative impact on a human organism, including a child organism at every stage of its development [1]. Smoking and exposure to ETS (Environmental Tobacco Smoke) increase a woman's risk of complications during pregnancy. These complications also affect the health of the fetus [2]. Samples of placenta collected for the studies had been prepared with the technique of accelerated solvent extraction, and later analyzed for the presence of thiocyanate ion and of selected ions, with the use of the technique of ion chromatography. The conducted studies have revealed that placenta is a very good biological material for the evaluation of the exposure of a woman and a fetus to toxic substances during pregnancy because it can be collected in a relatively non-invasive and simple manner, and it can be used for the evaluation of long-term exposure. The concentration of thiocyanate ion in 94% of placenta samples collected from active smokers was at a higher level than that in placenta samples of non-smoking women who were not exposed to the harmful compounds of tobacco smoke in the environment.. The high concentration of thiocyanate ions in the placenta samples proves that harmful substances from tobacco smoke penetrate the placenta.

References

[1] J.M. Rogers, J.M. *Reprod. Toxicol.*, 28 (2009) 152-160.
[2] J.A. Willford, L.S. Chandler, L. Goldschmidt, N.L. Day, *Neurotoxicol. Teratol.*, 32 (2010) 580-588.

Incorporation of endogenous olive oil compounds in olive oil w/o food nanoemulsions without co-surfactant and study of their properties and stability

M. Katsouli, V. Polychniatou and C. Tzia

Laboratory of Food Chemistry and Technology, School of Chemical Engineering, National Technical University of Athens, 5 Iroon Polytechniou St., 15780, Athens, Greece

E-mail: vpolychniatou@gmail.com

P3-05

In the present work the formation and the physicochemical properties of w/o nanoemulsion based on extra virgin olive oil were examined by incorporating endogenous compounds of olive oil with amphiphilic character, using non-ionic emulsifiers (Tween 20 and Tween 40), without the addition of co-surfactant. The studied endogenous compounds were: gallic acid, caffeic acid, quercetin, syringic acid, vanillic acid, and ascorbic acid. Initially pseudo-ternary phase diagrams (oil-water-emulsifier) were constructed in order to identify the ratios of the ingredients that can lead to stable nanoemulsions and determine the emulsifying ability of each endogenous component and emulsifier. Then nanoemulsions were prepared to permissible ratios as determined by the phase diagrams and the data acquired from the determination of their properties were processed. The effect of the endogenous compounds, emulsifiers, and their ratio were evaluated based on the mean diameter of the droplets, the emulsion stability, the turbidity, the viscosity and the color of the nanoemulsions. From the results of this study it was initially concluded that it is possible to prepare stable w/o nanoemulsions without the addition of co-surfactant. Furthermore it was proved that the addition of endogenous components of olive oil has positively influenced the properties of emulsions. Finally, the most effective type of endogenous component and emulsifier, and their optimum ratio in the system were determined.

Nanomaterials characterization by DLS, AF4-MALLS and SP-ICP-MS in consumer products

I. De La Calle[1,2] , M. Menta[2] , M. Klein[2], V. Vacchina[2] and F. Séby[2]

[1]Departamento de Química Analítica y Alimentaria, Universidad de Vigo, Vigo. Spain.
[2]UT2A, Pau, France.

E-mail: veronique.vacchina@univ-pau.fr

P3-06

The growth in the use of nanomaterials in consumer products seems unstoppable. In the case of cosmetics, nanoparticles (NPs) of titanium dioxide are allowed in sunscreens due to the properties as white pigment, and as UV blocker, it can also appear in toothpaste or shampoos. Similarly, NPs can be present in food such as silicon dioxide or Ag NPs.

In this work, a wide variety of drinks and cosmetics were tested by diverse techniques in order to evaluate the presence of nanomaterials (including bioparticles and metallic nanoparticles). The physico-chemical NPs characterization performed includes mean size, size distribution and chemical composition. This approach was performed as a quality control system to check the accomplishment of existing EU regulations for cosmetics for which the word "nano" should appear in the label as it is the case of titanium dioxide NPs [1] and for foods in which the presence of SiO_2 NPs is authorized [2] wheareas the use of Ag NPs in plastic food containers is not allowed [3].

For that purpose, a methodology was developed taking into account the sample preparation procedure and the operational conditions of each technique employed. Firstly, Dynamic Light Scattering (DLS) was employed for testing the sample preparation and sample stability. After that, Asymmetric Field Flow-Field Fractionation coupled with Multiangle Laser Light Scattering (A4F-MALLS) and Single Particle Inductively-coupled Plasma Mass Spectrometry (SP-ICP-MS) procedures were applied to evaluate the particle size of different metallic particles, respectively. Performances of each technique were evaluated and compared in order to be able to propose analytical methods allowing to meet compliance with the EU NPs regulation.

References

[1] COMMISSION REGULATION (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food. Off J Eur Union L (2009) 135/3– L 135/11.

[2] Union Guidelines on Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. Eur. Comm. Health Consum. Dir.-Gen. (2014).

[3] Commission of the European Communities (2011). Official Journal of the European Union. Art. 9. Directive EU/10/201, EC 2011.

Identification of superior ethanol tolerant industrial yeasts using droplet microfluidics

Y. Vervoort[1,2,3], R.S. Wiederkehr[3,4], T. Stakenborg[3], P. Fiorini[3], L. Lagae[3,4], K.J. Verstrepen[1]

[1] VIB Laboratory of Systems Biology, Gaston Geenslaan 1, B-3001 Leuven, Belgium
[2] CMPG Laboratory of Genetics and Genomics, KU Leuven, Gaston Geenslaan 1, B-3001 Leuven, Belgium
[3]Life Science Technologies, Imec, Kapeldreef 75, Leuven, Belgium
[4]Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200d, Leuven Belgium

E-mail: kevin.verstrepen@biw.vib-kuleuven.be

Fermentation industries (e.g. breweries or bioethanol companies) can optimize their industrial activities by applying Very High Gravity (VHG) fermentations, with high sugar contents and low nitrogen levels, instead of Normal Gravity (NG) fermentations. VHG fermentations are demanding specialized yeast cells which are able to cope with the high osmotic stress and ethanol concentration in the fermentation medium [1]. In principle, classic selection and breeding strategies allow generating superior yeasts for VHG fermentations. However, it is difficult to select the few superior variants amongst billions of inferior variants created by sexual crossing, hybridization and/or mutagenesis of existing yeasts. The only reliable way to assess a yeast's fermentation performance is to perform trial fermentations that mimic the desired industrial conditions, but this is difficult to do for more than a few candidates [2]. In this project, we use microfluidics to simultaneously encapsulate hundreds of single yeast cells in droplets (0.2 nl) and monitor their growth. Using a glass silicon chip (Fig 1), single yeast cells were distributed over droplets that were generated using a T-junction channel structure, from which the main channel contained oil and the side stream contained VHG medium. After droplet generation, droplets moved to an on-chip microreactor (Fig 1), where yeast growth easily could be visualized for ± 300 droplets. We optimized the oil-surfactant mixture in order to stabilize droplet fermentations for several days (Fig 2). The volume of droplets showing yeast growth decreased over time due to osmotic effects which allowed the identification of superior yeasts cells (Fig 3).

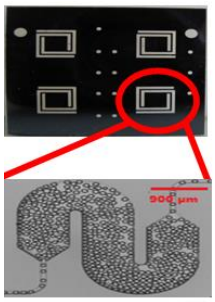


Fig 1 Microfluidics chip with four microcavities

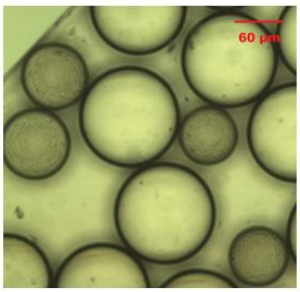


Fig 2 Fermented droplets surrounded by empty droplets with fresh medium

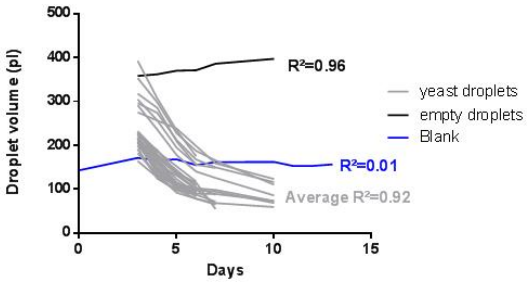


Fig 3 Droplet volume changes during fermentation due to osmosis

References

[1] Gibson, R., Lawrence, S.J., Leclaire, J.P.R., Powell, C.D. and Smart, K.A. *FEMS Microbial Rev* 31 (2007) 535-569

[2] Snoek, T., Picca Nicolino, M., Van den Bremt, S., Mertens, S., Saels, V., Verplaetse, A., Steensels, J. and Verstrepen, K.J. *Biotechnol Biofuels* 8 (2015) 32

A study of the determination of Co(II) by adsorptive stripping voltammetry at disposable screen–printed electrodes modified with a Bi precursor

M. Maczuga[1], A. Economou[2], A. Bobrowski[1] and M. Prodromidis[3]

[1] AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland
[2] Department of Chemistry, National and Kapodistrian University of Athens, Athens 157 71, Greece
[3] Department of Chemistry, University of Ioannina, Ioannina 451 10, Greece

E-mail: aeconomo@chem.uoa.gr

P3-08

Considerable research effort has been recently devoted to the task of developing new electrode materials that could potentially replace mercury in voltammetric analysis. Among such materials, different bismuth electrodes have gained prominence for trace metal detection by anodic stripping voltammetry [1].

Screen-printing is an attractive technology for the fabrication of electrochemical sensors enabling large–scale fabrication of low cost, reproducible and disposable electrodes with extended scope for modification [2]. Screen–printed bismuth–modified electrodes can be fabricated by electroplating a metallic film directly on the screen–printed carbon ink or by bulk–modification of the printing ink with a metal precursor (metal oxide or insoluble metal salt). The latter approach is attractive for the fabrication of complete sensors since the formation of the metallic film occurs *in situ* during the analysis [3].

This contribution is a proof–of–concept study on the use of screen–printed electrodes modified with bismuth citrate for the application in adsorptive stripping voltammetry using Co(II) as the target species in the presence of dimethylglyoxime as the complexing/adsorptive agent. Different parameters (such as the loading of the electrode with the precursor, the deposition potential and time, the concentration of dimethylglyoxime and further modification with a Nafion film) were investigated.

References

[1] C. Kokkinos and A. Economou, *Curr. Anal. Chem.*, 4 (2008) 183–190
[2] M. Li, Y.T. Li, D.W. Li and Y.T. Long, *Anal. Chim. Acta*, 734 (2012) 31– 44
[3] N. Serrano,A. Alberich, J. M. Díaz-Cruz, C. Ariño and M. Esteban, *TrAC*, 46 (2013) 15–29

Application of monolithic material for determination of iohexol in serum samples by capillary liquid chromatography

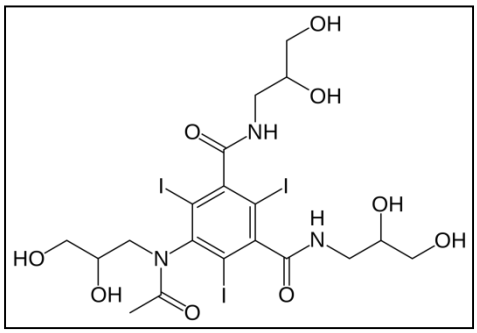
P. Chaisuwan[1,2], T. Chaloemsuwiwattanakan[3], D. Nacapricha[1,4], and P. Wilairat[1,5]

[1]Flow Innovation-Research for Science and Technology Laboratories (FIRST Labs.)
[2]School of Chemistry, Institute of Science, Suranaree University of Technology, 111 University Avenue, Muang District, Nakhon Ratchasima 30000, Thailand
[3]Department of Chemistry, Faculty of Science, Srinakharinwirot University, Sukhumvit 23 Rd, Bangkok 10110, Thailand
[4] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Rd, Bangkok 10400, Thailand
[5]National Doping Control Centre, Mahidol University, Bangkok, Thailand

E-mail: p.chaisuwan@sut.ac.th

P3-09

Iohexol is currently considered as a standard marker for determination of glomerular filtration rate due to its accurate estimation compared to other markers such as inulin or creatinine [1,2]. Liquid chromatography is the most common method used for quantitative analysis of iohexol in serum or plasma. To reduce the amount of solvents used in the chromatography, a porous monolithic material was prepared *in situ* in a fused silica capillary (id. 100 µm). Various monomers, polymerisation condition and mobile phase composition were investigated. Good separation in terms of efficiency and peak shape was achieved with chromatographic time of 5 min. This cost effective method was applied for the determination of iohexol in serum samples.



Chemical structure of iohexol (1-*N*,3-*N*-bis(2,3-dihydroxypropyl)-5-[*N*-(2,3-dihydroxypropyl)acetamido]-2,4,6-triiodobenzene-1,3-dicarboxamide).

References

[1] B. Frennby and G. Sterner, *Eur. Radiol*, 12 (2002) 475–484.
[2] E. Brändström,A. Grzegorczyk, L. Jacobsson, P. Friberg,A. Lindahl and M.Aurell, Nephrol. Dial. Transplant, 13 (1998) 1176–1182.

Microfluidic device integrated with screen printed graphene based-electrochemical sensor for glutathione detection

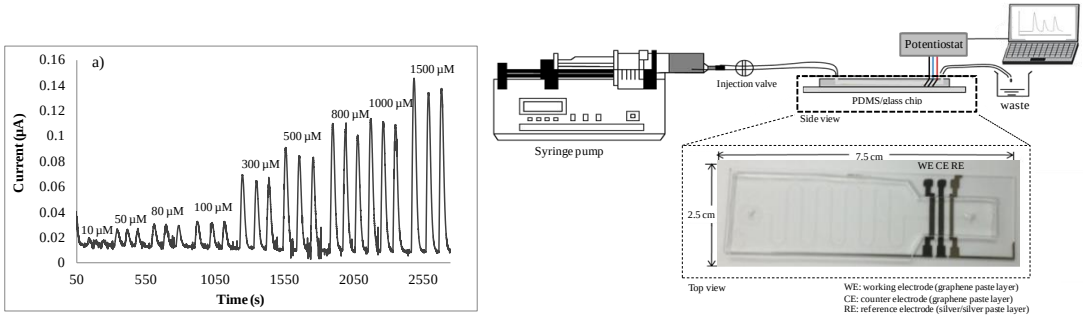
C. Karuwan[1,2], W. Pimpao[2], A. Wisitsoraat[2], T. Maturos[2], P. Chaisuwan[3], D. Nacapricha[1], and A. Tuantranont[2]

[1]Flow Innovative Research for Science and Technology laboratories (FIRST Labs.), Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Mahidol University, Rama VI Rd, Bangkok 10400, Thailand
[2]Thai Organic and Printed Electronics Innovation Center, National Electronics and Computer Technology Center, Klong 1, Paholyothin Rd, Pathumthani, Thailand 12120
[3]Department of Chemistry, Faculty of Science, Srinakharinwirot University, Bangkok, Thailand

E-mail: duangjai.nac@mahidol.ac.th, adisorn.tuantranont@nectec.or.th

P3-10

This work presents a new microfluidic device with integrated graphene-based electrochemical electrodes for in-channel amperometric detection. Graphene-based working and counter electrodes were fabricated by screen printing graphene paste on a glass substrate followed by screen printing of silver/silver chloride (Ag/AgCl) reference electrode. The screen-printed substrate was then bonded to prefabricated polydimethylsoloxane (PDMS) sheet containing microchannels via oxygen plasma treatment. The developed microfluidic device was then applied for glutathione analysis in pharmaceutical products. The method offers effective and fast glutathione detection with good analytical features including wide dynamic range (10-500 µM) and low detection limit (3 µM). In addition, the screen printed graphene electrode (SPGE) exhibits a good stability in microfluidic flow system and good repeatability for amperometric detection. The method has numerous advantages including low fabrication cost, high sensitivity, high throughput and satisfactory reproducibility. Thus, it holds great promise for advanced analytical applications.



References

[1] H. Becker, L.E. Locascio, Talanta, 56 (2002), 267–287
[2] C. Karuwan, A. Wisitsoraat, T. Maturos, D. Phokharatkul, A. Sappat, KJaruwongrungsee, T. Lomas, A. Tuantranont, Talanta 79 (2009) 995–1000.
[3] C. Karuwan, A. Wisitsoraat, D. Phokharatkul, C. Sriprachuabwong, T Lomas, D. Nacaprichab and A. Tuantranont, RSC Adv., 2013,3, 25792-25799

Determination of Sudan I in the presence of Sunset Yellow by adsorptive stripping voltammetry.

M. Gómez, V. Arancibia, C. Rojas and M. E. Aliaga

Facultad de Química, Pontificia Universidad Católica de Chile, Santiago, 7820436, Chile.

E-mail: mtgomez@uc.cl

P3-11

In recent years, the use of food additives in general and colours in particular have increasingly come under evaluation for their safety. Synthetic dyes are often added to foodstuffs and drinks in order to supply, intensify or restore their colour to create the desired coloured appearance. They present high stability to light, oxygen and pH, colour uniformity and lower production cost. Synthetic dyes can be classified into water soluble and fat soluble dyes based on their solubility. Only water soluble synthetic dyes are permitted in foods in some countries. Sunset yellow (SY) is a water soluble compound, allowed as a food coloring agent, whereas Sudan 1 is a fat soluble compound and may not be used because of its possible carcinogenieity. SY is a disulfo monoazo dye prepared by the coupling of diazotized 4-aminobenzenesulfonic acid with the sodium salt of 6-hydroxy-2-naphthalenesulfonic acid. During their manufacture, sudan I (SI), 1-(phenylazo)-2-naphthalenol, may be produced by the diazotization and coupling of aniline, an impurity in technical and refined sulfanic acid, with 2-naphthol [1,2].

Adsorptive stripping voltammetry (AdSV) is a useful technique to determine organic compounds since it combines excellent sensitivity, selectivity, accuracy and precision with low instrumentation cost. The sensitivity and selectivity depend on the working electrode. Despite the toxicity of mercury, the hanging mercury drop electrode is a nearly ideal electrode, especially for cathodic processes and mainly due to good adsorptive properties. The present study describes an adsorptive stripping procedure for SI determination in spiked soft drinks containing SY. Varying the pH the signals of SI and SY were separated obtaining the best resolution between pH 11.5 to 12.7 and the highest peak current for SI to a pH 12.7. The chosen E_{ads} was −0.30 V and t_{ads} of 30 s. In these conditions the signal of SI is observed at −0.69 V and the SY at −0.57 V. The relationship between the peak current and both dyes concentration is linear in the 2.5–30.0 μg L^{-1} range. The detection limit was found to be 4.3 μg L^{-1} for SI and 2.0 μg L^{-1} for SY (30 s). The method was validated by determining spiked SI in a soft drink containing SY (Gatorade orange), obtaining 46.13 ± 2.14 μg L^{-1} (0.4 %). At present, we are looking for the presence of SI in other foods containing SY. The presence of SI in real samples will be confirmed by HPLC-MS/MS-MS/MS.

***Acknowledgements*:** This work was supported by FONDECYT Postdoc Grant #3150196, FONDECYT Grant #1130081 and FONDEQUIP EQM130032

References

[1] C. Tatebe, T. Ohtsuki, N. Otsuki, H. Kubota, K. Sato, H. Akiyama, Y. Kawamura, *Am. J. Anal. Chem*. 3 (2012) 570-575.

[2] B.R. Petigara, A.L. Scher, *J. Aoac Int.* 90 (2007) 1373-1378.

Study of the Interaction of 4-Nitrobiphenyl with DNA at a Hanging Mercury Drop Electrode

E. Horakova, V. Vyskocil and J. Barek

Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ-128 43 Prague 2, Czech Republic

E-mail: eva.horakova@natur.cuni.cz

P3-12

Differential pulse voltammetry and cyclic voltammetry at a hanging mercury drop electrode (HMDE) were used to study the interaction of 4-nitrobiphenyl (4-NBP) with double-stranded low molecular weight DNA in buffered solution. The mechanism of the electrochemical reduction of 4-NBP was studied as well, using cyclic voltammetry at HMDE. Moreover, the calibration dependence of the peak current of 4-NBP on the concentration of DNA in aqueous solution was constructed to be used for the indirect determination of DNA, based on the fact that the peak current of 4-NBP is decreasing with increasing concentration of DNA in solution.

Reaction kinetic parameters, such as electron transfer coefficient, α, rate constant, k_0, and diffusion coefficient, D, can be determined using voltammetric techniques and chronocoulometry in order to investigate whether the presence of DNA influences the electrochemical kinetics of 4-NBP or not. From the change of the peak current of 4-NBP, the equilibrium constant, β_S, the binding constant, K, and the binding number, m, of the supramolecular complex (4-NBP–DNA) can be determined.

This research was carried out within the framework of the Specific University Research (SVV260205). Financial support from the Grant Agency of the Czech Republic (Project P206/12/G151) is gratefully acknowledged.

Electrochemical biosensors based on minireactors with various types of amalgam and silica powders for flow systems

O. Josypčuk, B. Josypčuk

J. Heyrovsky Institute of Physical Chemistry of AS CR, v.v.i.
Dolejskova 2155/3, 182 23 Prague, Czech Republic

E-mail: josypcuk@jh-inst.cas.cz

P3-13

Sensitivity of the enzyme biosensor depends on the area covered by the enzyme. Classical solid detection electrodes have a relatively small surface which can be enlarged by the use of an enzymatic reactor (ER). The reactor is commonly placed in flow system in front of the detector. In this case, the biosensor consists of two separate parts: the enzymatic reaction takes place in the reactor and the detector then registers either some product of enzymatic reaction or, e.g., decrease/increase of oxygen concentration in the solution [1]. Amperometric detection is carried out in a flow-through cell with silver solid amalgam (AgSA) tubular detector [2] or in a wall-jet cell with a polished AgSA electrode prepared in a chromatographic capillary or in a joint. High hydrogen overvoltage on the amalgams allows to work in aqueous solutions up to –2 V [3]. Such negative potentials can be achieved only with mercury electrodes. The very useful advantage of solid amalgams is the possibility to prepare electrodes of required size and shape. The enzymatic reactor is fabricated from a PTFE tube (commonly, length 22 mm, inner diameter *ID* = 1.59 mm). *ID* of this tube is the same as the outer diameter of a standard chromatographic capillary. At both ends of the Teflon tube, two 6 – 8 mm long silicone tubes were fixed. These tubes seal the inlet and outlet capillary with the reactor body. The prepared reactor (length 10 mm) has volume of 19.1 µl and can be used immediately. Incorporation of the reactor into the flow system is very easy and fast. The reactor is filled by some powder covered by an enzyme. The powder can be of silver solid amalgam or of various forms of silica. Long-term stability of the biosensor is ensured by anchoring the enzyme to the surface of the amalgam or silica by covalent bonds. The preparation procedure of the biosensors is universal and is suitable for binding various proteins or other compounds containing $–NH_2$ group. Enzymes ascorbate oxidase, glucose oxidase, catalase, tyrosinase and laccase were used to test the biosensors. Statistical results of parallel measurement with model solutions of the different analytes with all fabricated biosensors show their high accuracy and sensitivity.

References

[1] B. Josypčuk, J. Barek, and O. Josypčuk, *Anal. Chim. Acta*, 778 (2013**)**, 24-30.
[2] O. Yosypchuk, J. Barek, and B. Yosypchuk, *Electroanalysis*, 24 (2012**)**, 2230-2234.
[3] B. Yosypchuk and J. Barek, *Crit. Rev. Anal. Chem.*,39 (2009**)**, 189-203.

Acknowledgements: This work was financially supported by Grant Agency of the Czech Republic (Grants P206/11/1638 and P208/12/1645).

Application of the general system of phenomenological peak models construction

S.V. Romanenko, E.V. Larionova

Tomsk Polytechnic University

E-mail: evl@tpu.ru

P3-14

The analytical peak modeling has been the subject of interest among chemists in recent decades. Phenomenological simulation of peak-shaped analytical signals applies at the development of algorithms of data treatment with aim of validity and correctness verification. On the other hand phenomenological models can be directly used in the signal processing algorithms (resolution of overlapped signals, base line correction etc.) and multivariate data analysis (MCR-ALS for example) as well.

A great number of analytical peak functions have been described in literature. In same cases these functions does not satisfy the requiremens of analysts to universality, adequacy and simplicity. Moreover lack of methodology of choosing of the appropriate peak function for the experimental analytical signals makes difficult their application. We propose a principally novel approach to the phenomenological modeling of peaks. We have early proposed the general system of phenomenological peak functions construction [4, 37]. Having reviewed a lot of publications, we distinguished three main elementary peaks – Gaussian peak, peak of the logistic function derivative and Cauchy peak. System of phenomenological peak function construction bases on combinations and modifications of these peaks. We propose four common independent types of modifications (two symmetric and two asymmetric) and three types of combination (additive combination and two types of multiplicative combination) of symmetrical normalized peaks with peak normalization preserved. We also demonstrate two general principles of peak construction, which allowed building peaks with necessary properties on the basis of simpler functions.

We can generate thousands of models with help of this system of peak construction. So our next goal is to show how to discriminate models and choose the appropriate models for the voltammetry, chromatography and spectroscopy signals. Peak shape analysis should be preliminary carried out by the contour technique [1]. We determined peak shape variation ranges in the each separate case. So the group of appropriate peak functions can be chosen. Then we carried out the approximation of experimental peaks (voltammetry, chromatography and spectroscopy) and founded the most adequate phenomenological functions.

In conclusion we show the different ways of application of phenomenological functions. Simulation for the goals of data treatment algorithms investigation will be demonstrated. We also show application of phenomenological functions in the algorithm of resolution of overlapped peaks (curve fitting and MCR-ALS), base line and systematic errors correction in voltammetry and spectrophotomery methods.

References

[1] S. V. Romanenko, A. G. Stromberg, T. N. Pushkareva, *Anal. Chim. Acta*, 580 (2006) 99–106.

[2] S. V. Romanenko, A. G. Stromberg, Modelling of analytical peaks, *Anal. Chim. Acta*, 581 (2007) 343–354.

Potentiometric biosensing applications using lab-made electrochemical sensors based on lipid stabilized films in contact with two different nano-electrodes

G. -P. Nikoleli[1], V. N. Psychoyios[1], N. Tzamtzis[1] and T. Varzakas[2]

[1]Laboratory of Inorganic & Analytical Chemistry, School of Chemical Engineering, Dept 1, Chemical Science, National Technical University of Athens, GR-15780 Athens, Greece
[2]Dept of Food Technology, Technological Ed. Institute of Kalamata, Greece

* Correspondence Author: E-mail: gnikoleli@gmail.com

P3-15

A novel potentiometric cholesterol biosensor was constructed through the immobilization of cholesterol oxidase on stabilized polymeric lipid membrane onto graphene electrode. The polymeric lipid membrane has been prepared using cholesterol oxidase along with lipid providing enhanced sensitivity, selectivity, electrical signal transfer communications and molecule capturing. The presented biosensor reveals an appreciable reproducibility, good selectivity and high sensing capability with a linear slope curve of ~64 mV per decade. The possibility of the practical use of the biosensor was investigated using cholesterol solution and real blood serum samples [1]. A novel potentiometric uric acid biosensor was also constructed by immobilizing uricase into stabilized lipid films using zinc oxide (ZnO) nanowire electrodes. Uricase was incorporated into the lipid film prior polymerization on the surface of well aligned ZnO nanowires resulting in a sensitive, selective, stable and reproducible uric acid biosensor. A rapid response time was observed over the whole concentration range with 95 % of the steady state voltage achieved within 6 s with a sensitivity of ca. 31 mV/decade for a sensor electrode without the lipid film membrane and 61 mV/decade with the lipid film. Figure 1 shows recordings obtained during FIA experiments. The sensor response had no interferences from ascorbic acid, glucose, urea, proteins and lipids [e.g. interferent to analyte = 1000 : 1] [2].

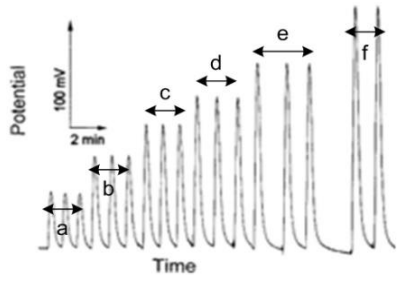


Figure 1. Recordings obtained during FIA experiments, for the detection of a uric acid solution, giving reproducible signals corresponding to the following concentrations: a: 1.00 μM; b: 5.00 μM; c: 10.0 μM; d: 50.0 μM; e: 100 μM; and f: 1000 μM.

References

[1] G. –P. Nikoleli, Z. H. Ibupoto, D. P. Nikolelis, V. Likodimos, N. Psaroudakis, N. Tzamtzis, M. Willander and T. Hianik, *Cent. Eur. J. Chem.*, 11 (2013) 1554-1561.
[2] N. Tzamtzis, V. N. Psychoyios, G. -P. Nikoleli, D. P. Nikolelis, N. Psaroudakis, M. Willander and M. Q. Israr, *Electroanalysis*, 24 (2012) 1719-1725.

Effect of pyrrolidine dithiocarbamate and diethyl dithiophosphate on the determination of arsenic by adsorptive stripping voltammetry.

C. Núñez and V. Arancibia

Pontificia Universidad Católica de Chile. Chemistry Faculty. Vicuña Mackenna 4860. Macul, Santiago de Chile. Phone: 56(2)6864723

E-mail: ctnunez@uc.cl

P3-16

Arsenic contamination has been identified as a public health problem worldwide because it has serious toxic effects even at low exposure levels. Natural processes and anthropogenic activities are triggers of arsenic emission and that may be mobilized in the surface. Intense efforts are devoted to developed methods for the detection of arsenic species and mitigation of effect depends on chemical forms and oxidation states. Electrochemical methods for arsenic determination are considered as an alternative to the other analytical techniques because of their sensitivity, mainly adsorptive stripping voltammetry. The use of Cu or Se has been increasing the sensitivity and selectivity in the determination of As, because As^{3+} can react with these metals to form intermetallic complexes, Cu_xAs_y or Se_xAs_y, which can be preconcentrated on the mercury electrode and then stripped cathodically [1,2].

The main objective of this work was to study complexing agents such as ammonium diethyl dithiophosphate (ADDTP) and ammonium pyrrolidine dithiocarbamate (APDTC) with the purpose to obtain detection limit lowest and to avoid the oxidation of As^{3+} to As^{5+}. Accordingly, studies of experimental parameters were made to select the best conditions to ensure the highest possible sensitivity and precision for each method. The results showed that the presence of ligand plays an important role improving the signal current of As^{+3}. On the other hand, when CPB was added the peak current of As^{+3} increased and then decreased slightly. Table 1 showing the best experimental conditions for both ligands. Furthermore, were determined analytical figures of merit for to compare the methods. Thereby, was select APDTC because it was obtained detection limit lowest and better reproducibility. Hence, peak current is proportional to As concentration over the 0.5–5.0 μgL^{-1} range, with a 3σ LOD of 0.08 μgL^{-1}. Under these working conditions, Ni, Li, Co until 500 μgL^{-1}, and Se until 50 μgL^{-1} no interferences were found. The method was validated using water spiked with As^{3+} and was used to determine total arsenic in river water from the Calama area in the North of Chile.

Table1. Optimum experimental parameters each ligand.

	Cu [mgL^{-1}]	HCl [$molL^{-1}$]	Ligand [$\mu molL^{-1}$]	CPB [$\mu molL^{-1}$]	T_{ads} [s]	E_{ads} [V]	PA [V]
ADDTP	40	2.0	1.00	2.6	60	-0.30	0.20
APDTC	60	1.5	0.01	5.2	80	-0.40	0.20

The authors acknowledge gratefully the financial support of FONDECYT under Regular Project 1130081and CONICYT under PhD scholarship 21130492.

References

[1] V. Arancibia, A. Lopez, M. Zuñiga and R. Segura, *Talanta*, 68 (2006) 1567-1573.
[2] M. Ferreira, A. Barros, *Anal. Chim. Acta* 459 (2002) 151-159.

Chiral Cavity Ring-Down Polarimetry: New methods for ultrasensitive measurements of chirality

A. Papadaki, D. Sofikitis, A. Spiliotis, G. Katsoprinakis, B. Loppinet, T.P. Rakitzis

Department of Physics, University of Crete, 71003 Heraklion-Crete, Greece, and IESL-FORTH, N. Plastira 100, 71110 Heraklion-Crete, Greece

P3-17

Sensing chirality is of fundamental importance to many fields. The most widely used methods for optical chiral sensing are the traditional methods of circular dichroism and optical rotation. However, these chiral signals are typically very weak, and their measurement is limited by larger time-dependent backgrounds (such as spurious birefringence) and by imperfect and slow subtraction procedures. We present proposals [1] and demonstrations [2] of a pulsed-laser bowtie-cavity-ringdown polarimeter with counter-propagating beams, which solves these background problems: the chiral signals are enhanced by the number of cavity passes (typically $>10^3$); the effects of linear birefringence are suppressed by a large induced intracavity Faraday rotation; and rapid signal reversals are effected by reversing the Faraday rotation and subtracting signals from the counter-propagating beams. These advantages allow measurements of absolute chiral signals in environments where background subtractions are not feasible. Specifically, we measure optical rotation from of (+)-□-pinene and (–)-□-pinene in open air, as well as from chiral liquids in the evanescent wave produced by total internal reflection at a prism surface. Evanescent-wave optical rotations of various (+)-maltodextrin and (–)-fructose solutions confirm the Drude-Condon model for Maxwell's equations in isotropic optically active media [2]. The improved sensitivity and background subtraction procedures should improve chiral sensing in many fields.

References

(1) L. Bougas, G. Katsoprinakis, W. von Klitzing, J. Sapirstein, T.P Rakitzis, "Cavity-enhanced parity non-conserving optical rotation in metastable Xe and Hg", *Phys. Rev. Lett.* **108**, 210801 (2012).
(2) D. Sofikitis, L. Bougas, A. Spiliotis, G. Katsoprinakis, B. Loppinet, T.P. Rakitzis, "Evanescent-wave and ambient chiral sensing by signal-reversing cavity-ringdown polarimetry" *Nature* **514**, 76 (2014).

Acid-base properties of the pH indicators into polymethacrylate matrix

N. Gavrilenko[1], N. Saranchina[1], A. Sukhanov[1], I. Mikheev[2] and M. Proskurnin[2]

[1]Tomsk Polytechnic University, Tomsk, Russia
[2]Moscow State University, Moscow, Russia

E-mail: gavrilenko@mail.tsu.ru

P3-18

Monitoring and eventually maintaining of pH plays important role in inviromental, industrial and biomedical applications. Due to a broad range of applications pH measurements the development of new ways of pH determination are attractive field of instrumental methods of analysis. The conventional electrochemical methods of pH measurements have known limitation: susceptible to electrical interference, size, rigid design [1]. Optical chemical sensors deprived of such limitations.

In general the main part of reagent-based optical pH sensor consists of support (matrix) and immobilized pH sensitive reagent. In present work PMM was used for immobilization pH indicators and their acid-base properties in PMM studied. PMM is a specially created material containing functional groups which provide ability to extract both the reagent and determined substance [2]. Transparent PMM plates (thickness, 0.60±0.04 mm) were prepared by radical block polymerization of methacrylate monomers. Next, these plates were cut as 6.0 × 8.0 mm working platelets (weight, ca. 0.05 g). The representatives several classes (azo- and sulfonephthalein indicators) of traditional pH indicator dyes were used for immobilization. The immobilization of reagents into the polymethacrylate matrix was performed by adsorption from water and water-alcohol solutions under batch conditions. To do that, 10–25 mL of a reagent solution was stirred with a PMM for 1–15 min. Investigation of acid-base equilibrium of immobilized reagent carried out by solid-phase spectrophotometry.

It is found that immobilization of pH indicators into PMM lead to change of maximum wavelength of absorption of both base and acid forms of pH indicators. The pK_a of the indicators immobilized into PMM were determined and compared with the pK_a of the indicators in solution. The immobilization of pH indicators into PMM enabled to extend the pH indicating range compared with solution and to act as colorimetric pH sensors.

This work was partly supported by Russian Science Foundation (project 14–19–00926).

References

[1] D. Wencel, T. Abel and C. McDonagh, *Analytical chemistry*, 86 (2014) 15-29.
[2] N. Gavrilenko and G. Mokrousov, Patent 2272284 (RU), 2004.

The transparent of optical sensors PEG-PMMA on xanthene dyes

N. Gavrilenko, N. Saranchina, M. Gavrilenko

Tomsk Polytechnic University, Tomsk, 634050, Russia

E-mail: gavrilenko@mail.tsu.ru

Poly(methyl methacrylate) (PMMA), one of the commonly used polymers, is widely used to fabricate optical analytic systems. Bulk modification is an effective way to improve the new analytical properties while retaining the transparent of the polymer. Various modifications of the PMMA matrix have been using in different techniques like optical chemical sensor, physical adsorption, biomolecule adsorption, chemical modification and so on. The introduction of polyethylene glycol (PEG) into the PMMA has attracted considerable attention as a means of minimizing sorption, because of their low interfacial energy, non-adhesive property and high diffusion mobility. The technique described [1] where PEG was immobilized into polymethylmethacrylate matrix (PMM).

Combine polymer having a PMMA backbone and hydrophilic PEG chains, has been synthesized and applied for the design of transparent colour sensors. The properties of the modified PMMA such as transparent, analytical functionality and sorption properties are characterized by various techniques. The sorption of xanthene dyes into polymer bulk is a central concern in our system in which materials contact with fluids.

The IR- and visible spectra shows the good sorption properties for xanthene dyes by polymer with 1% PEG and the lower one with 20% PEG. Between 2 and 5% of PEG the transparence degree drops with increasing amount of PMMA whereas the amount of adsorbed rhodamine increases. Such nonspecific adsorption behavior of the PMMA-PEG could be mainly attributed to the flexible hydrophilic PEG chains in the bulk where transparent matrix could easily interact into the aqueous solutions. It was found that polymer matrixes, which have only weak enthalpic interactions with the xanthene dyes, show strong sorption of xanthene dyes irrespective of the details of the chemical composition.

If the amount of adsorbed rhodamine as well as the transparence degree is plotted to the percentage of PEG in the polymer matrix, an inverse correlation between the colour and the rhodamine adsorption can clearly be seen. At the point when the transparence degree drops from around 2.4 % PEG the adsorption changes simultaneously to xanthene dyes adsorbing behavior .With increasing amount of the PEG chains the polymer becomes more hydrophilic and the transparence of the polymer increases.

The transparent optical sensors for xanthene dyes adsorption must be used in the field of technology for sensors, catalysis, analytics and drug discovery. Last but not least xanthene dyes sorption is of utmost importance for the monitoring of oil fields.

References

[1] M.A. Gavrilenko, M.S. Burmetieva and N.A. Gavrilenko, *Advanced Materials Research,* 1040 (2014) 437-441.

Monitoring methodology of selected groups of VOCs in industrial wastewater – a review

G. Boczkaj, P. Makoś, M. Momotko, D. Chruszczyk, A. Fernandes

Department of Chemical and Process Engineering, Chemical Faculty, Gdansk University of Technology, 80-233 Gdansk, 11/12 Narutowicza Str., Poland

E-mail: grzegorz.boczkaj@gmail.com

P3-20

As a result of industrial processes, i.e. the paper industry, textile, brewing, food processing, refining and tanning industry, wastewater containing large amounts of volatile organic compounds (VOCs) are formed. Depending on the type of feedstock processed the wastewater may contain a different groups of volatile organic compounds, including oxygenated (O-VOCs), nitrogen-containing (VNCs) and sulphur-containing (VSCs) volatile organic compounds. The occurrence of these compounds even at low concentrations affects a significant odor nuisance and may negatively affect the health of the people living around industrial plants.
There are a variety of analytical methods, which differ in terms of metrology and utility, which allows to monitor the content of VOCs in industrial wastewater. Currently, the most popular technique for the determination of all groups of VOCs is gas chromatography with universal detectors, i.e. MS and FID. Selective detectors, ensuring low detection thresholds for the VSCs are flame (FPD) and pulsed flame (PFPD) photometric detector and chemiluminescence detector (SCD). For VNCs a nitrogen-phosphorus detector (NPD), surface ionization detector (SID), nitrogen chemiluminescence detector (NCD) are used. For O-VOCs oxygen selective detector a so-called O-FID is used. Other selective detectors may be used for all of the compounds after derivatization of analytes. When applying methods based on liquid chromatography mainly reversed phase high performance liquid chromatography (RP-HPLC) is used. It is possible to quantify a large number of compounds from the group of VOCs at concentrations of the μg/L (ppb) order. Applications of CE and IC or IExC, are limited to the detection of phenols and carboxylic acids. Other methods such as electrochemical sensors and spectrophotometric methods are limited to the determination of only the major components of the sample. For quantification at very low concentration levels, appropriate sample preparation techniques are necessary.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Science Center, Warsaw, Poland – decision no. DEC-2013/09/D/ST8/03973.

The potentialities of atomic absorption techniques based on the high-resolution continuous source for environmental analysis

M.Yu. Sinitsyn, A.G. Borzenko

Chemical Department, Moscow State University, Moscow, 119991, Russian Federation

E-mail: AGBorzenko2009@yandex.ru

The method of atomic absorption spectroscopy (AAS) remains one of the most applicable methods for the elemental analysis due to its sensitivity and selectivity. Detection limits without preconcentration achieve 10^{-5}-10^{-7}% (depending on theelement and atomization technique). Traditional way of realization of atomic absorption elemental analysis is based on Walsh approach. Its concept consists of using the line radiation sources (hollow cathode lamp, HCL), modulation of the radiation and the use of a selective amplifier tuned to the same modulation frequency. This concept guarantees the well-known selectivity and specificity of AAS. At the same time conventional AAS has some disadvantages. One of the main disadvantage is the impossibility of realization of multielement analysis and problems concerning background correction and spectral interferences.

One of the ways to solve the foregoing problems is using new conception based on the high-resolution continuum source AAS combined with a specially developed high-resolution double monochromator. The new concept uses a specially developed xenon short-arc lamp as a continuum source with very high radiation intensity, especially in the UV range, a high-resolution double monochromator with a prism pre-monochromator and an echelle grating monochromator with active wavelength stabilization and a UV-sensitive CCD linear array detector with a few hundred pixels that make visible the entire spectral environment of the analytical line.

Since the intensity of radiation in the AAS technique has no influence on the sensitivity but does influence on the noise, the detection limits with HR-CS AAS are improved by a factor of 2-5 on average. Using a linear array detector makes it possible to measure the absorbance not only in the line core but also on the line wings. As a result the dynamic working range can be extended to 5-6 orders of magnitude without any problems. Naturally all spectral lines are fully available as well, i.e. also lines of elements for which no line sources (HCL) are available. An absolutely novel feature is also the possibility of using absorption lines of di-atomic molecules such as PO or CS for the element determining (such as phosphorous or sulfur). Our contribution is devoted to comparison of analytical possibilities of the atomic absorption techniques based on hollow cathode lamp and high-resolution continuous source for analysis of different samples (aluminum and nickel alloys, steels and soil). The estimation of detection limits and other metrological characteristics for both techniques has been made. The merits of HR-CS AAS (reduction of detection limits, widening of calibration ranges of elements to be determining, decreasing/elimination spectral interference influences) have been demonstrated. The experimental results obtained will be presented and discussed in detail.

This work is supported by the Russian Foundation for Basic Researches (RFBR) project № 15-03-05853

Continuous Measurement of Water Soluble Components of Atmospheric Aerosols

P. Mikuška, L. Čapka, A. Kořínková and Z. Večeřa

Institute of Analytical Chemistry of the ASCR, v. v. i., Veveří 97, 602 00 Brno, Czech Republic

E-mail: capka@iach.cz

P3-22

Measurement of chemical composition of aerosols is presently performed mostly by sampling of aerosols at filter-packs or impactors with subsequent off-line analysis. Alternatively, on-line aerosol collectors based on a condensation of steam on particles are used [1,2,3]. Another approach is applied in aerosol collector called Aerosol Counter-flow Two Jets Unit (ACTJU), where a deionized water at room temperature instead of steam is employed for the continuous sampling of atmospheric aerosol particles [4]. The ACTJU collector under optimum conditions collects quantitatively aerosol particles down to 0.3 μm in diameter while the collection efficiency of smaller particles decreases.

To increase the sampling efficiency even for aerosol particles smaller than 300 nm, the current ACTJU version was combined with a water-based condensation growth tube (GT) located upstream of the ACTJU sampler. The GT is composed of two parts, cooled and heated [5]. During passing through the first part of GT, the analysed air with small particles are cooled while in the second part of GT the cooled mixture is admixed with heated water vapour. Small particles are exposed to vapour supersaturation, which activates condensational growth, subsequent rapid condensational growth due to condensation of water vapour enlarges small particles to larger sizes in the supermicrometer range and formed droplets are then easily collected in the ACTJU sampler. The collector effluent is permanently sucked out from the ACTJU for subsequent on-line analysis of particulate water-soluble species.

The collection efficiency of GT/ACTJU sampler measured under optimized conditions was 98-100% for aerosol particles in the size range 10-200 nm and the particle number concentration of 10^3-10^5 P/cm^3. A sampling of aerosol particles on parallel filter was used as a reference method.

References

[1] P.K. Simon and P.K. Dasgupta, *Anal. Chem.*, 67 (1995) 71-78.
[2] A. Khlystov, G.P. Wyers and J. Slanina, *Atmos. Environ.*, 29 (1995) 2229-2234.
[3] R.J. Weber, D. Orsini, Y. Daun, Y.N. Lee, P.J. Klotz and F. Brechtel, *Aerosol Sci. Technol.*, 35 (2001) 718-727.
[4] P. Mikuška and Z. Večeřa, *Anal. Chem.*, 77 (2005) 5534-5541.
[5] S.V. Hering, M.R. Stolzenburg, F.R. Quant, D.R. Oberreit and P.B. Keady, *Aerosol Sci. Technol.*, 39 (2005) 659-672.

A Portable Device for Fast Analysis of Explosives in the Environment

L. Čapka[1], Z. Večeřa[1], P. Mikuška[1], J. Šesták[1], V. Kahle[1] and A. Bumbová[2]

[1]Institute of Analytical Chemistry of the ASCR, v. v. i., Veveří 97, 602 00 Brno, Czech Republic
[2]University of Defence, Kounicova 65, 662 10 Brno, Czech Republic

E-mail: capka@iach.cz

P3-23

Explosives belong to the very specific group of environment contaminants. Their presence is typically located in the areas after military training and wartime activities. The other sources of contamination include the manufacturing, testing and disposal of explosives [1,2].

Detection of explosives is the subject of many investigations by law enforcement agents and forensic scientist. The identification and discrimination of evidence taken from crime scenes is a common practice in forensic investigations. The higher demands on simple and fast determination of hazard materials or strange objects are required in connection with worldwide often repeated terrorist activities.

Present paper describes the fast and sensitive method for the analysis of explosives in the environment using the novel portable device, that is assembled from the automated microcolumn liquid chromatograph [3,4], photolytic converter and miniaturized chemiluminescence detector with selective response [5].

The device is able to determine selectively nitramine- and nitroester- and most of nitroaromates-based explosives as well as inorganic nitrates at trace concentrations in water or soil extracts in less than 8 minutes without previous preconcentration procedures. Because of internal power supply, the device ensures 12 hours of continuous operation. Limits of detection of compounds of interest are in the range of concentrations from 5.0×10^{-9} M to 8.0×10^{-5} M for a signal-to-noise ratio of 3.

Table 1: Determinated explosives with limits of detection [M]

nitrate	7.5×10^{-7}	TNT	5.0×10^{-6}
HMX	5.0×10^{-9}	2,4-DNT	8.0×10^{-5}
RDX	1.5×10^{-8}	2,6-DNT	8.0×10^{-5}
NG	1.5×10^{-7}	TNB	7.1×10^{-6}
EGDN	1.5×10^{-7}	DNB	1.3×10^{-5}
PETN	3.8×10^{-7}	NB	3.2×10^{-5}
Tetryl	8.1×10^{-9}	DMDNB	9.4×10^{-7}

References

[1] N. Pon-Saravanan, S. Venugopalan, N. Senthilkumar, P. Santhosh, B. Kavita and H. Gurumallesh-Prabu, *Talanta*, 69 (2006) 656-662.
[2] D.A. Cassada, S.J. Monson, D.D. Snow and R.F. Spalding, *J. Chromatogr. A*, 844 (1999) 87-95.
[3] M. Krejčí and V. Kahle, *J. Chromatogr.*, 392 (1987) 133-142.
[4] J. Šesták, F. Duša, D. Moravcová and V. Kahle, *J. Chromatogr. A*, 1276 (2013) 26-32.
[5] P. Mikuška, L. Čapka, Z. Večeřa, I. Kalinichenko and J. Kellner, *Int. J. Environ. Anal. Chem*., 94 (2014) 1038-1049.

Influence of surface tension of simulated pulmonary fluids on bioavailability of metals in urban aerosol and vehicle exhaust

P. Coufalík[1], P. Mikuška[1], K. Křůmal[1], M. Vojtíšek[2], T. Matoušek[1] and Z. Večeřa[1]

[1]Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Veveří 97, 602 00 Brno, Czech Republic
[2]Faculty of Mechanical Engineering, Czech Technical University in Prague, Technická 4, 166 07 Prague, Czech Republic

E-mail: coufalik@iach.cz

P3-24

Increasing environmental burden in urban agglomerations including metals from fuels combustion, traffic and industry, poses considerable health risks. The aim of this research was to evaluate the bioavailability of selected metals contained in emissions from engines and urban aerosol. To assess the degree of potential intoxication by inhalation way, the extraction in solutions of simulated pulmonary fluids was chosen. Generally, extractants used for these studies vary considerably in their chemical composition. A key factor in the successful simulation of metal release from particles in the alveoli is a sufficiently low surface tension of the solution. Dipalmitoyl phosphatidylcholine (DPPC) is the main substance for surface tension reducing [1].

Samples of emissions from biofuels and urban aerosols (collected for heating and non-heating season) were subjected to extraction in six extractants and mineralization for the determination of total metal contents. Bioavailable proportions obtained by the extraction in Gamble's solution, Gamble's solution with DPPC and artificial lysosomal fluid (ALF) [2] were compared with the results of extraction in deionized water, saline and newly proposed simulated lung surfactant which is based on DPPC and physiological concentration of calcium ions in the alveoli [3]. Trace concentrations of metals in extracts were determined by means of ICP-MS. Simulated pulmonary fluids evinced significantly different extraction efficiency for each element. A higher ionic strength of extraction solution or a lower surface tension of the solution had no clear effect on increase in extraction efficiency. Equilibrium of the extraction is probably dependent on concentration gradient between the sample and the extractant.

Acknowledgement

This work was supported by Grant Agency of the Czech Republic under grant No. 503/13/1438S and by Institute of Analytical Chemistry of the ASCR, v. v. i. under an Institutional research plan No. RVO: 68081715.

References

[1] O. Blanco and J. Pérez-Gil, *Eur J Pharmacol*, 568 (2007) 1-15.
[2] W. Stopford, J. Turner, D. Cappellini and T. Brock, *J Environ Monit*, 5 (2003) 675-680.
[3] W. Ganong, *Review of Medical Physiology*, McGraw-Hill, New York (2001).

A Universal Analyzer for Large Volume Preconcentration of Nanomolar Iron(II) from Seawater on Renewable Sorbent

B. Horstkotte, P. Chocholouš, P. Solich

[1]Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Králové,
Charles University in Prague, Heyrovského 1203, Czech Republic

E-mail: Horstkob@faf.cuni.cz

P3-25

A simple yet versatile Lab-on-Valve [1] configuration for preconcentration of large sample volumes is presented. Confluent mixing for in-line addition of loading buffer inside the holding coil and re-cycling of the eluate for chromogenic reaction was demonstrated. The system was applied to the determination of iron(II) in acidified seawater using 1,10-phenanthroline as color reagent. A novel cellulose based HQ8 resin was used for in-system packing of a microcolumn showing excellent retention behavior and loading capacity.

Using a FIALab3500 instrument, the syringe pump was used for handling all solutions (loading buffer, eluent, and color reagent) and HQ8 resin slurry, while the peristaltic pump integrated was used for continuous sample provision during microcolumn loading. Instrumental modifications include a 14 cm long laboratory made detection glass cell and in-line degasification and bubble trapping to suppress spontaneous carrier degasification.

The flow-through port was advantageously used to keep the eluted analytes for re-aspiration for subsequent chromogenic reaction. I.e., a universal preconcentration procedure was developed, which can be combined with other analytical reagents.

Among the studied parameters were the compositions, volumes, and flow rates of loading buffer, eluent, and reagent, as well as the microcolumn size, repeatability, and stability of operation. Excellent reproducibility of < 5 %, a LOD of < 15 nmol/L, analysis frequency of 12 h^{-1}, linearity up to 1 µmol/L for 3.3 mL sample as well as applicability to real samples were demonstrated.

The work was supported by the Czech Ministry of Education, Youth and Sports project VES13 Kontakt II LH13023 and the European Social Fund and state budget of Czech Republic, TEAB, Project CZ.1.07/2.3.00/20.0235. BH and PC are thankful for the financial support from Charles University in Prague by Project PRVOUK P40/1105, Charles University Research Centre (UNCE 204026/2012).

References

[1] J. Růžička, *Analyst*, 125 (2000) 1053–1060.

Optimizing the determination of antimony, arsenic and chromium in drinking water by graphite furnace atomic absorption spectrometry

N. Tziarou, E. Kaprara and M. Mitrakas

Lab of Analytical Chemistry, Chemical Engineering Department, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

E-mail: manasis@eng.auth.gr

P3-26

Graphite furnace atomic absorption spectrometry (GFAAS) is one of the most common analytical methods that may be used for accurate and precise determination of antimony (Sb), arsenic (As) and chromium (Cr) at low concentrations (< 10 μg/L) in drinking water. However, the above mentioned elements present more than one valance states in water, which may influence the method's accuracy. This study is aiming to evaluate and quantify the influence of elements' valence state, as well as the carbon tube's configuration on the sensitivity of the method. For this purpose, different calibration curves were obtained for trivalent and pentavalent form of Sb and As, as well as for Cr(III) and Cr(VI) using standard (open-ended) and end-capped transversely heated graphite atomizer (THGA) tubes.

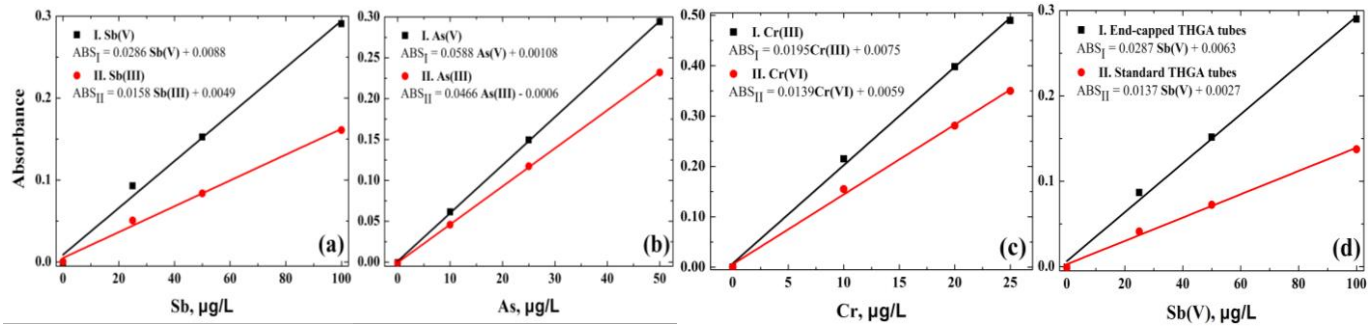


Figure 1. Sb(V) vs Sb(III) calibration curves **(a),** As(V) vs As(III) calibration curves **(b)**, Cr(III) vs Cr(VI) calibration curves **(c),** Sb(V) calibration curves for end-capped vs standard THGA tube **(d).**

Comparing the slope of the calibration curves for the two different forms of Sb (Fig. 1a), it was concluded that Sb(V) was measured with much greater (nearly twice) sensitivity. That also counted for As(V) (Fig. 1b) and Cr(III) (Fig. 1c) but with a less significant difference in the two species determination. This divergence in absorption for the two oxidation states of Sb, As and Cr indicated that these elements must be present solely in specific valence state in order to establish high accuracy determination.

The method's evaluation by practicing a standard THGA tube vs an end-capped showed that the latter significantly improved sensitivity of Sb(V) determination (Fig.1d), as well as the corresponding of As(V) and Cr(III). This improvement on the studied elements' detection limits when end-capped tube was used should probably be attributed to lower diffusion rate of atomic vapour due to tube's optimum configuration.

Application of in-situ passive flux samplers (PFSs) in the field of estimating the emission flux of volatile organic compounds emitted from laminated wood-based materials and floor coverings

M. Marć[1], J. Namieśnik[1] and B. Zabiegała[1]

[1]Department of Analytical Chemistry, Gdansk University of Technology, Gdansk, Poland

E-mail: marcel.chem@gmail.com

P3-27

According to literature data portable analytical devices classified as the passive flux samplers (PFS) can be successfully applied in the process of non-destructive estimating of the emission flux of VOCs and SVOCs emitted to the indoor air from various types of indoor and finishing materials. The in-situ passive flux samplers are small-sized analytical devices typically made of glass (clear or tinted), stainless steel or plastic materials with an internal diameter of a few centimetres in which sorption medium is installed inside the PFS body. The sorption medium for analyte samples collection from gaseous phase installed inside analytical device can be in the shape of a disc placed on the entire upper surface of the device (like an inverted Petri dish) or a tube/container filled with sorption bed positioned in a horizontal or vertical position. The transport of organic compounds emitted from the surface of indoor material in the direction of sorption bed installed inside the chamber takes place on the principle of molecular diffusion according to the first Fick's law of diffusion. The working time of this type of passive analytical devices installed in indoor environment ranges from 30 minutes to 24 hours [1-4].
The construction of two types of home made in-situ passive flux samplers made of stainless steel or plastic material has been presented. The home made in-situ PFSs were used to estimate the emission flux of volatile organic compounds (mainly BTEX compounds and monoterpenes) emitted from laminated wood-based materials and floor coverings installed inside the indoor environment. As a sorption medium for analyte samples collection from gaseous phase, the tube made of stainless steel net filled with sorption bed Carbograph 4 was installed inside the chamber. At the stage of liberation of analytes from sorption medium, the two-stage thermal desorption technique was applied. The separation, identification and quantitative determination of analytes was carried out using GC-MS system.

The scientific work was financially supported by Ministry of Science and Higher Education within "Iuventus Plus" project in years 2015 - 2017, project number IP2014 028373

References

[1] M. Marć, B. Zabiegała, J. Namieśnik, *Trends Anal Chem*, 32 (2012) 76-86
[2] M. Marć, B. Zabiegała, J. Namieśnik, *Crit Rev Anal Chem*, 43 (2013) 55-61
[3] N. Shinohara, Y. Kai, A. Mizukoshi, M. Fujii, K. Kumagai, Y. Okuizumi, M. Jona, Y. Yanagisawa, *Build Environ*, 44 (2009) 859-863
[4] D. H. Kang, D. H. Choi, S. M. Lee, M. S. Yeo, K. W. Kim, *Build Environ*, 45 (2010) 1816-1825.

The estimation of total volatile organic compounds emissions generated from peroxide cured natural rubber/polycaprolacone blends

K. Formela[1], M. Marć[2], J. Namieśnik[2] and B. Zabiegała[2]

[1]Department of Polymers Technology, Gdansk University of Technology, Gdansk, Poland
[2]Department of Analytical Chemistry, Gdansk University of Technology, Gdansk, Poland

E-mail: kformela.ktp@gmail.com

P3-28

Development and research in the field of biodagradable polymeric materials result in their diverse applications in industry (e.g. eco-package, medicine, automotive, etc.). Estimated data indicated that production of "biopolymers", will grow at the rate 30% per year [1]. Therefore, searching for new biodegradable polymers with unique properties gaining interest among science and industry representatives.

Preparation of polymer blends is commonly known production method of new polymeric materials, including biodegradable polymers [2, 3]. However, usually weak interfacial interactions between components result in unsatisfactory mechanical properties of the blends, what limits their usage. To prevent this technological difficulties the most of polymer blends require further compatibilization, which enhance their properties.

One of the simplest and the most efficient methods of polymer blends compatibilzation is cross-linking. Free radicals formed during curing process may react in two opposite directions. First main reaction is the desired formation of new bonds between two (or more) separate polymeric phases. On the other hand, some degradation (mainly by main chain scission) may occur.

During presented work natural rubber/polycaprolacone (NR/PCL) blends were cured using organic perioxide. The effect of NR/PCL blends curing conditions on the emission of total volatile organic compounds (TVOCs) was estimated using headspace analysis combined with gas chromatography with flame ionization detector (HS-GC-FID technique). For better understanding the interactions between used components, correlation between TVOCs parameters and static mechanical properties of obtained polymeric blends were determined.

The scientific work was partially financially supported by Ministry of Science and Higher Education within "Iuventus Plus" project in years 2015 - 2017, project number IP2014 028373

References

[1] L. Shen, J. Haufe and M.K. Patel, *Product Overview and Market Projection of Emerging Biobased Plastics*. Report No: NWS-E-2009-32 (2009) The Netherlands: Utrecht.
[2] L. Yu, *Biodegradable Polymer Blends and Composites from Renewable Resources* (2009), John Wiley & Sons, Inc., Hooboken, New Jersey.
[3] A. Sionkowska, *Progress in Polymer Science*, 36 (2011) 1254-1276.

Tar composition in biogas depending on gasification conditions

S. Osipovs

Department of Chemistry, Daugavpils University, Daugavpils, LV-5401, Latvia

E-mail: sergejs.osipovs@du.lv

P3-29

The aim of the present research is to find out if the difference in gasification conditions the concentration of tar in the produced synthesis gas. For research, the two Circulating Fluidised Bed gasifiers situated in eastern Latvia (Rēzekne region) were chosen. The gasifiers differ in the diameter of their reactors, temperature, hence the difference in the conditions of biomass gasification in them. Chinese tea waste was employed as biomass.

Tar was sampled at the producer gas temperature reaching 250°C. In the present work, a solid-phase adsorption (SPA) method for determining concentration of tar compounds has been chosen. The sampling device consists of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal. The sampling volume is 100 – 200 mL.

In the gasifier with a smaller reactor diameter, the total tar concentration is bigest than in the gasifier with a larger reactor diameter. The resulting composition of tar contains Benzene, Naphthalene, Acenaphthylene, and over 27 other compounds.

It is concluded that less total tar and lower range of volatile organic compounds such as Benzene were obtained in the latter case, whereas percentage of the heavy tar is higher.

Determining the isotopic composition of nitrate in sediments in the gulf of Riga

S. Osipovs[1], A. Skute[2] and D. Vardanjans[2]

[1] Department of Chemistry, Daugavpils University, Daugavpils, LV-5401, Latvia
[2] Armgate Ltd., Marupe, Riga District, LV-2167, Latvia

E-mail: sergejs.osipovs@du.lv

P3-30

Denitrification is the most important mechanism of nitrogen loss in the ocean. The dissimilatory reduction of nitrate exhibits a significant organism-level nitrogen isotope fractionation, with ^{14}N-bearing nitrate being preferentially consumed by the denitrifying organism, leaving the residual nitrate pool enriched in ^{15}N. Thus, the isotopic composition of marine nitrate can be used to identify denitrifying environments and, when combined with ocean circulation and nutrient data, can provide quantitative constraints on regional denitrification rates.

Nitrogen and oxygen isotope ratios of nitrate provide a powerful tool to investigate nitrate sources and cycling mechanisms. The analysis of nitrate for both $\delta^{15}N$ and $\delta^{18}O$ allows improved discrimination among potential sources and reaction mechanisms.

In our time, $\delta^{15}N–NO_3^-$ and $\delta^{18}O–NO_3^-$ in nitrate can be measured according to three analytical methods: two 'denitrifier methods' requiring Isotope Ratio Mass Spectrometry (IRMS) analysis of N_2O gas generated by bacterial or chemical means, and a procedure known as the 'ion-exchange resin method' whereby NO_3^- is extracted from freshwater and converted into solid silver nitrate that is analysed by IRMS. Minor modifications have been adopted by some to ease the sample preparation, one of the most significant changes being the precipitation of O-bearing contaminants (mainly sulphate and phosphate) with barium chloride prior to passing water through an anion-exchange resin so that $AgNO_3$ is ready for both $\delta^{15}N$ and $\delta^{18}O$ analyses.

Heavy metal pollution of pond sediments

K.S. Patel[1], N.S. Dahariya[1], Y. Nayak[1], N.K. Jaiswal[2], L. Matini[3], L. Borgese[4], A. Gianoncelli[4] and E. Bontempi[4]

[1]SOS in Chemistry, Pt. Ravishankar Shukla University, Raipur, India
[2]Department of Chemistry, ITM University, Raipur, India
[3]Department of Exact Sciences, Marien Ngouabi University, Brazzaville, Congo
[4]INSTM and Chemistry for Technologies Laboratory, University of Brescia, Italy

E-mail: patelkhageshwarsingh@gmail.com

P3-31

Ponds, standing water reservoirs contain shallow water with aquatic plants and animals in the tropics. In urban area of India, the ponds are contaminated by pollutants i.e. nutrients, metals, organic pollutants, etc. [1-2]. Heavy meals are one of the major serious pollutants in our natural environment due to their toxicity, persistence and bioaccumulation problems [3]. Toxic heavy metals entering the ecosystem may lead to bio-accumulation and bio-magnifications [4]. In the present work, the contamination of pond sediment of three industrial cities: Raipur, Bhilai and Korba of central India (21° 13′ 12″ N, 82° 40′ 48″ E) with the heavy metals are described. The total reflection X-ray fluorescence spectrophotometeric (TXRF) technique was used for monitoring of the metals in 17 pond sediments. The concentration of Ti, V, Cr, Mn, Ni, Cu, Zn, Pb and As was ranged from 2714–8121, 45–175, 100–392, 127–2595, 31–77, 32–89, 36–626, 7–32 and 7–150 mg/kg with mean value of 4459±577, 89±15, 168±36, 1095±348, 49±6, 55±8, 135±61, 22±3 and 44±7 mg/kg, respectively. The concentration of Ti, Mn and Pb was found to decrease with increasing depth profile (0 – 30 cm) of the sediment. However, the concentration of V, Ni, and Cu and As was increased with increasing depth profile. The concentration variations, correlation, sources, enrichment and toxicity of the heavy metals are discussed.

References

[1] S. K. Sarkar, A. Binelli, C. Riva, M. Parolini, M. Chatterjee, A. K. Bhattacharya, B. D. Bhattacharya, K. K. Satpathy, Organochlorine Pesticide Residues in Sediment Cores of Sunderban Wetland, Northeastern Part of Bay of Bengal, India, and Their Ecotoxicological Significance**,** *Archives of Environmental Contamination and Toxicology*, 55(2008) 358-371.

[2] S. B. Saha, A. Mitra, S. B. Bhattacharya and A. Choudhury, Status of sediment with special reference to heavy metal pollution of a brackish water tidal ecosystem in northern Sundarbans of West Bengal, *Tropical Ecology*, 42(2001) 127-132.

[3] N. F. Y. Tam and Y. S. Wong, Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution*, 110(2000) 195-205.

[4] K. Zabetoglou, D. Voutsa and C. Samara, Toxicity and heavy metal contamination of surficial sediments from the Bay of Thessaloniki (Northwestern Aegean Sea) Greece. *Chemosphere*, 49(2002) 17-26.

Investigation of the adsorption of gaseous pollutants into various aquatic environments at different temperatures

D. Sevastos, A. Koliadima

Chemistry Department, University of Patras, 26504 Patras Greece

E-mail: akoliadima@upatras.gr

P3-32

The interaction between gaseous pollutants and aquatic environment is important for studying pollution effects in the earth's water systems. For this purpose Reversed – Flow Gas Chromatography (RFGC) is applied for investigating the SO_2 and NO_2 adsorption into triply distilled water and artificial sea water. A commercial gas chromatograph equipped with an appropriate detector (FPD or TCD) depending on the kind of pollutant under study, is required to apply RFGC. The experimental arrangement is very simple and the traditional gas chromatograph is slightly modified to include a T-shape cell constructed from glass or stainless steel chromatographic tube inside the chromatographic oven, and a four- or six port gas valve inside or outside the oven. The diffusion column, connected perpendicularly to the sampling column at its midpoint, contains only stagnant carrier gas (nitrogen), which also flows through the empty sampling column, either from D_1 to D_2 or vice versa. At the free end of the diffusion column, a small glass vessel filled with the liquid under study was connected. The sampling column is devoid of any solid or liquid material, and, for separation purposes, an additional separation column is placed before the detector (Fig.1). After injecting a small amount of the pollutant a continuous elution elution curve was recorded. By the mean of the four – port valve the direction of the carrier gas was reversed for time shorter than the gas hold-up time and narrow symmetrical chromatographic peaks called ´´sample peaks´´ were created (Fig.2). The height of these peaks is proportional to the concentration of the pollutant at the junction point $z = 0$ and $x = l'$ of the sampling column at time t.

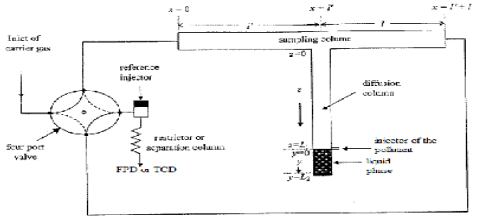


Fig. 1. Experimental arrangement.

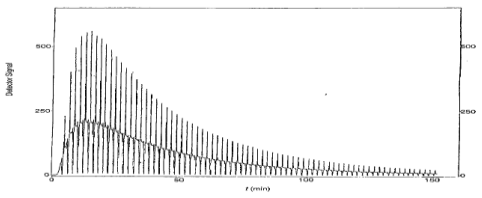


Fig.2 A reversed-flow gas chromatograph for the interaction between SO_2 and 3D water at 313,15 K

Using an appropriate mathematical analysis the physicochemical parameters such as diffusion coefficient of the gaseous pollutant in the water, D_L, the rate constant for the chemical reaction of the pollutant with the water, k_R, and the distribution coefficient for the gaseous pollutant, $K = K_L / K_g$, between the water and the carrier gas phase can be calculated. From the results the dependence on the temperature as well as on the nature of the aquatic environment of all physicochemical parameters can be investigated and the mechanism for the adsorption of gaseous pollutants can be extracted.

New environmental and biological reference materials for persistent organic pollutants such as PAHs and PCBs compounds

M. Słomińska, B. Zabiegała, G. Bajger-Nowak, M. Marć, P. Konieczka, J. Namieśnik

Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

E-mail: korpala.m@poczta.onet.pl

P3-33

Taking into account the current trends in analytical chemistry, a project of preparation of reference materials (MODAS) has been established. New reference materials will be an important complement to the current offer of certified reference materials available on the market and offered by leading centres and institutions (NIST, IRMM). Production of new reference materials is particularly significant due to the their representativeness - commercially available reference materials (soils, sediments) do not fully meet the expectations of Polish laboratories, due to other origins, different geochemical characteristics and anthropogenic pollution, which limits their applicability and usefulness in Polish laboratories.
The studies include the preparation of biological and environmental reference materials dedicated for the PAHs and PCBs compounds analysis.
The project include preparation of reference materials in the form of soil and biological tissues (cod, cormorant) with certified concentration of organic compounds from the groups of PCBs and PAHs. For each samples the procedures for simultaneous determination of PAHs and PCBs has been developed.
The research procedure for preparation of reference materials is presented in the Figure 1.

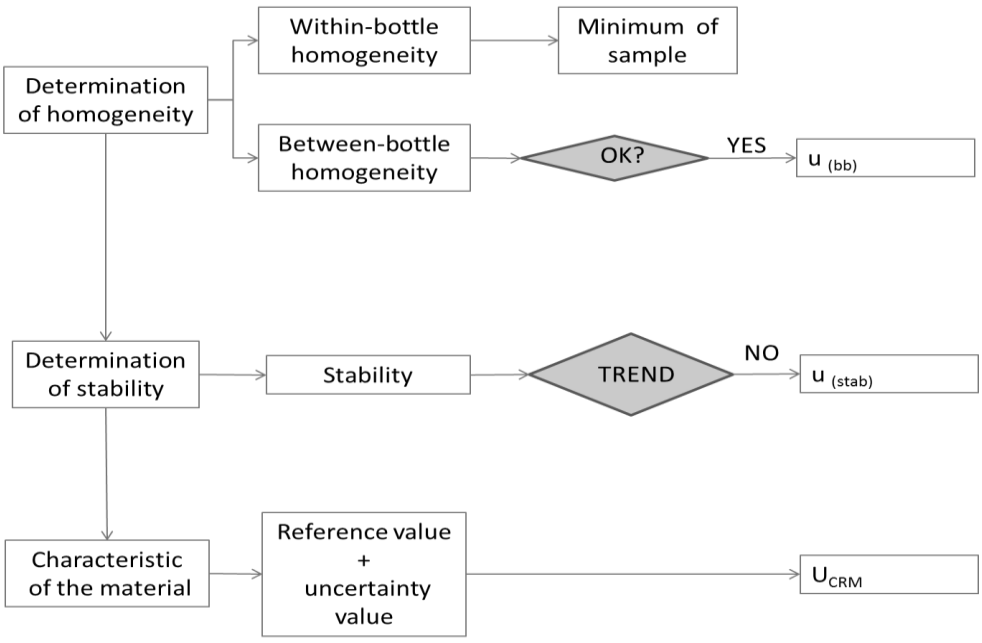


Fig.1. The research procedure for preparation of reference materials.

Determination of Lead in Drinking Water: Exploring the Potential of In-Syringe Analysis for Automation of Direct-Immersion Single-Drop Microextraction

I. Šrámková, B. Horstkotte, K. Fikarová, H. Sklenářová, P. Solich

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

E-mail: srami5aa@faf.cuni.cz

P3-34

Since its introduction by Maya et al. [1], In-Syringe Analysis (ISA) has proven to be an advantageous tool for the automation of various analytical methodologies. Homogenous solution mixing without additional external chambers as well as automation of dispersive liquid-liquid microextraction can be achieved using magnetic stirring [2]. Applications with solvents, both lighter [2] and heavier [3] than water, have been reported. Recently, also the automation of head-space single drop microextraction was demonstrated [4].

In this work, a different mode of SDME was automated. As a model analyte, lead in drinking water was determined using the reaction with dithizone. The employed system was very compact, comprising a 5 mL syringe, a nine-port selection valve and a spectrophotometric detector with optic fibres connected to 1 cm flow-path detection cell.

The physical and chemical parameters such as stirring rate, extraction time, volumes and concentrations of the buffer, reagent, and interference masking solution as well as the composition and volume of the extraction solvent were thoroughly studied. The effect of interferences was studied in concentrations relevant to their occurrence in drinking water. The developed method offers a simple, compact and precise (RSD < 5 %) protocol for lead determination in drinking waters, with a sample throughput of 12 h^{-1}.

The optimization of the method, final operational protocol will be discussed. A linear range up to 1 µM and a detection limit of 50 nM were achieved. The effect of the masking solution on the interferences and results of real samples measurements will be presented.

The authors acknowledge the project of specific research No. SVV 260 184 and the Grant Agency of the Charles University, project No. 1316213.

References

[1] F. Maya, J. M. Estela, V. Cerda, *Anal. Bioanal. Chem*., 402 (2012) 1383-1388.
[2] B. Horstkotte, R. Suarez, P. Solich, V. Cerda, Anal. Chim. Acta, 788 (2013) 52-60.
[3] B. Horstkotte, R. Suarez, P. Solich, V. Cerda, Anal. Methods, 6 (2014) 9601-9609.
[4] I. Šrámková, B. Horstkotte, P. Solich, H. Sklenářová, *Anal. Chim. Acta*, 828 (2014) 53-60.

Automated control monitoring of the content of pH, Cl^--, NO_3^-- ions in the wastewater by ionometry

A.G. Kagirov, A.N. Vtorushina, D.A. Kalashnikova

Tomsk Polytechnic University, Lenina avenue, 30, Tomsk, 634050, Russia

E-mail: anl@tpu.ru

P3-35

According to the changes in legislative framework of the Russian Federation in the field of environmental protection factories need to lower a level of negative impact on water objects.

In this regard, creation of analytical complexes for monitoring of qualitative and quantitative parameters of industrial wastewaters is an actual task.

Monitoring process of wastewaters parameters before and after cleansing actions generally is carried out manually nowadays. Sampling, sample preparation, carrying out an analysis, elaboration demand certain time resources and high qualification of the staff. Therefore, one of the main requirements to modern monitoring systems is possibility of the automated process of keeping track of water environment parameters.

At this stage of development of physical and chemical methods of the analysis in relation of the cost of the analysis and possibility of its full automation the most interesting are the following methods: a conductometry, a potentiometry, photocolorimetry [1], coulometric titration, solid-phase spectrophotometry on the polymethylmethacrylate matrix [2].

The list of controlled parameters in water objects is rather wide and regulated by standards. In this work the possibility of automation of potentiometric determination an ion-selective electrodes of such water environment parameters as a pH value, chloride-, nitrate-, ammonium ions concentration is considered.

The design of the measuring instrument supposes its installation into flowing system. Measurement of the above listed parameters is implemented by the combined sensors with an ion-selective indicated electrodes.

Ion-selective electrodes can be fail is broken down because of due to mechanical impurity or decrease of membrane selectivity. Operability of electrodes is estimated by change of the slope of a calibration curve.

In this work the possibility of ion-selective electrodes calibration construction is considered, by using system of required ions electrogeneration in the immediate measured environment. For an elimination of mechanical impurity the system of hydraulic flushing by the environment in which measurement of the monitored parameters is carried out.

Therefore the offered design will allow to perform autocalibration of sensors and to estimate the content of the defined components in the monitored solution.

References

[1] Ari Ivaska. Comprehensive Analytical Chemistry, 54 (2008) 441–459.
[2] Gavrilenko N.A., Saranchina N.V., J. of Analytical Chemistry, 64 (2009) 226-230.

Solid phase extraction of lead by a nanosized urchin-like $NiCo_2O_4$ adsorbent prior to determination FAAS

E. Yavuz[1], Ş. Tokalıoğlu[1], H. Şahan[1,2] and Ş. Patat[1]

[1]Erciyes University, Faculty of Science, Chemistry Department, TR-38039, Kayseri, Turkey
[2]Erciyes University, Nanotechnology and Research Center, TR-38039, Kayseri, Turkey

E-mail: eyavuz@erciyes.edu.tr

P3-36

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for heavy metals removal from aqueous systems. This is partly because of their large surface areas and high activities caused by the size quantization effect. Recent studies suggested that many NMOs exhibit very favorable sorption to heavy metals in terms of high capacity and selectivity, which would result in deep removal of toxic metals to meet increasingly strict regulations. They are present in different forms, such as particles, tubes and others. The size and shape of NMOs are both important factors to affect their adsorption performance. In recent years, these materials have been proposed and used in the preconcentration of trace metals due to their high surface area, high adsorption capacity and high chemical activity [1,2].

In this study, nanosized urchin-like $NiCo_2O_4$ adsorbent was synthesized and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). $NiCo_2O_4$ as a promising mixed-metal oxide has been widely investigated for potential applications in lithium-ion batteries, supercapacitors, electrocatalysts, and optoelectronic devices [3]. The nanosized urchin-like $NiCo_2O_4$ was used for the first time as an adsorbent for the preconcentration of the Pb(II) ions in various samples. The effect of experimental parameters such as pH, contact time, eluent type and volume, sample volume, adsorption capacity and matrix effect was investigated. pH was found to be 4. The elution was easily made with 2 mL of 2.5 mol L^{-1} HCl. The recovery values for Pb(II) were found to be ≥90% in the presence of 10000 mg L^{-1} Na(I), 10000 mg L^{-1} K(I), 5000 mg L^{-1} Mg(II) and 7500 mg L^{-1} Ca(II).

References

[1] M. Hua, S. Zhang, B. Pan, W. Zhang, L. Lv and Q. Zhang, *Journal of Hazardous Materials*, 211-212 (2012) 317-331.
[2] E.Yavuz, Ş.Tokalıoğlu, H. Şahan and Ş. Patat, *Talanta*, 115 (2013) 724-729.
[3] X. Y. Yu, X. Z. Yao, T. Luo, Y. Jia, J. H. Liu and X. J. Huang, *ACS Applied Materials & Interfaces*, 6 (2014) 3689-3695.

Separation and pre-concentration of beryllium from street sediment and water samples by tannic acid functionalised graphene aerogel prior to GFAAS determination

E. Yavuz[1], Ş. Tokalıoğlu[1], H. Şahan[1,2] and Ş. Patat[1]

[1]Erciyes University, Faculty of Science, Chemistry Department, TR-38039, Kayseri, Turkey
[2]Erciyes University, Nanotechnology and Research Center, TR-38039, Kayseri, Turkey

E-mail: eyavuz@erciyes.edu.tr

P3-37

Compounds of beryllium are very toxic. It can enter into human's body and result in cancer. The beryllium concentration in tap or surface water should not exceed a limit 0.2 μg L^{-1}. However, average beryllium contents in most natural waters are by orders of magnitude below this level in the ng L^{-1} range. Different techniques have been used for the determination of beryllium. These include spectrophotometry, spectrofluorimetry, atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry [1-3]. However, due to matrix of the samples and low levels of this element, an efficient separation and preconcentration method is required. In comparison with traditional techniques, solid phase extraction offers several advantages. Recently, carbon based nanomaterials have attracted the attention of scientific community due to their novel properties like large surface area, long range of porosity, good thermal stability and good mechanical strength. Graphene, the latest member of the carbon family is believed to be one of the most interesting materials of this century. As the large delocalized π-electron system of graphene can form strong π -stacking interaction with the benzene ring [4].

In this study, tannic acid functionalised graphene aerogel (TFGA) was synthesized and characterized. The TFGA was used for the first time as an effective adsorbent for the preconcentration of the Be(II) ions in various samples prior to graphite furnace atomic absorption detection. pH was found to be 6. The recovery values for Be(II) were found to be ≥91% for 5000 mg L^{-1} Na(I), 7500 mg L^{-1} K(I), 7500 mg L^{-1} Mg(II) and 7500 mg L^{-1} Ca(II) ions. 3 min vortexing time was enough for both adsorption and elution. 2 mL of 2.0 mol L^{-1} HCl was used for elution. The described method was validated with certified reference materials (TMDA 70 lake water and SPS-WW1 Batch111-Wastewater) and spiked real samples.

References

[1] A. Afkhami, T. Madrakian, A. A. Assl and A. A. Sehhat, *Analytica Chimica Acta*, 437 (2001) 17–22.
[2] J. L. Burguera, M. Burguera, C. Rondon, P. Carrero, M. R. Brunetto and Y. P. Pena, *Talanta*, 52 (2000) 27-37.
[3] S. R. Yousefi, F. Shemirani, M.R. Jamali and M.S.-Niasari, *Microchimica Acta*, 169 (2010) 241-248.
[4] E. Yavuz, Ş. Tokalıoğlu, H. Şahan and Ş. Patat, *RSC Advances*, 3 (2013) 24650-24657.

Automation of drug transport monitoring using sequential injection manifold

L. Zelená[1], E. Lopes[2], M. Segundo[3], M. Miró[4], L. Hyršová[5], P. Pávek[5], H. Sklenářová[1]

[1]Department of Analytical Chemistry, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Akademika Heyrovskeho 1203, 550 05 Hradec Kralove, Czech Republic
[2]Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua Campo Alegre 687, 4169-007 Porto, Portugal
[3]Department of Chemical Sciences, Faculty of Pharmacy, University of Porto, Rua de Jorge Viterbo Ferreira 228, 4050-313 Porto, Portugal
[4]FI-TRACE group, Department of Chemistry, University of Balearic Islands, Cra. de Valldemossa, km 7.5, 07122 Palma de Mallorca, Spain
[5]Department of Pharmacology and toxicology, Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Akademika Heyrovskeho 1203, 550 05 Hradec Kralove, Czech Republic

E-mail: zelenal@faf.cuni.cz

P3-38

In vitro permeation studies are one of the methods widely used in clinical research in evaluation of drug interaction with membrane transporter proteins or drug-drug interactions. These tests are performed using cellular monolayers seeded on a semi-permeable membrane of commercially produced inserts. Solution of the tested drug is applied to apical chamber and the interactions are evaluated following the permeation to the basolateral chamber. Aim of this work was to build a universal set-up for automation of drug transport monitoring to get more detailed kinetic profile of the permeation. The system was based on a sequential injection (SI) manifold connected to the liberation unit, a Franz diffusion cell (FDC). The measuring procedure consisted of: aspiration of the sample from basolateral compartment of FDC (BL-FDC), on-line fluorometric detection of sample and re-filling of aspirated volume to the BL-FDC with fresh solution. In the performed assays, rhodamine 123 (Rho123) was used as a marker of P-glycoprotein (P-gp) membrane transporter function. At first, the SI system connected with single FDC was built. This system enables sampling every 10 min and get more detailed kinetic profile of the marker transport. This approach showed the possibility to automate this test, but it was time consuming when repetitions of the measurements had to be carried out for precise evaluation. The second system was based on connection of the SI manifold with three FDC in parallel. This set-up enables to perform 3 measurement in real time but due to sample aspiration, detection and refilling steps between sampling from each FDC, time intervals had to be prolonged to 30 min. As an additional step, a simple separation was added before sample detection where short C18 precolumn (0.50 mm, 0.46 μm high-resolution monolith, Merck) was connected between the selection valve and the detection flow cell. This approach enables to distinguish fluorescence signals of a marker (Rho123) and tested substances working as inhibitors of P-gp (verapamil and quinidine were observed).
The systems will be described in detail and experimental data will be presented with respect to evaluation of kinetic profiles of just Rho123 or both substances under the study.

The authors gratefully acknowledge financial support of the Grant Agency of the Charles University, project GAUK No. 159415, and by the project of specific research, SVV no. 260 184.

Physical and Chemical Characteristics of a typical Greek Refuse Derived Fuel

D. Bakirtzis, P. Danias, C. Michalopoulos, V. Tsapara and S. Liodakis

National Technical University of Athens School of Chemical Engineering
Laboratory of Inorganic and Analytical Chemistry, 9 Heroon Polytechniou Str, 15780 Athens
tel: +30210772316 Fax: +302107723377

E-mail: d.bakirtzis@hotmail.com

P3-39

It is a rather common place, in our days that fossil fuels are decreasing rapidly. This need -in addition with landfill saturation- leads us to search and develop for new solid fuels. The term 'Refuse Derived Fuel (RDF)' has no official definition, hence it is interpreted differently across countries. RDF usually refers to the segregated high calorific fraction of Municipality Solid Waste, commercial or industrial process wastes [1]. In an effort to understand RDF pyrolysis and combustion behavior four (4) chemical parameters: total chlorine (% dry base) with EN 15408, humidity (%) with CEN/TS 15414-1:2010, ash content (% dry base) EN 15403:2011 and calorific value (kcal/g) with EN 15400, in forty four (44) samples from Greek installation in the larger area of Attica has been measured regularly during the first six (6) months of 2015. Chlorine, draw major attention because it induces high temperature corrosion and low efficiency in waste-to-energy plants. Chlorine can be found almost in a wide range of material, such us non-packaging plastics (dry basis), polyvinylchloride (PVC) from packaging, electrical wire insulation etc. High amounts of chlorine have been detected to the typical Greek RDF. This is due to the addition of materials into RDF blended mass (PVC, PE, PA6 mostly found at packing materials) in an effort of the installation production line to increase calorific values [1,4]. RDF calorific value has a vital role in the trading value of the material and the financial robustness of the plant. Humidity must always be monitored, as it reduces the calorific value of RDF, and brings implications i.e. co-incineration to cement plants [2,4]. Finally, the ash content of RDF constitutes a significant amount of weight; hence a mass residue management and an eco-friendly utilization is compulsory [2,3].

References

[1] S. Peddireddy, P.J. Longhurst, S.T. Wagland, Characterizing the composition of waste-derived fuels using a novel image analysis tool ,Waste Management, Volume 40, June 2015, Pages 9-13
[2] Chunguang Zhou, Weihong Yang, Effect of heat transfer model on the prediction of refuse-derived fuel pyrolysis process ,Original Research Article Fuel, Volume 142, 15 February 2015, Pages 46-57
[3] Anouk Bosmans, Christopher De Dobbelaere, Lieve Helsen ,Pyrolysis characteristics of excavated waste material processed into refuse derived fuel, Original Research Article Fuel, Volume 122, 15 April 2014, Pages 198-205
[4] Shuhn-Shyurng Hou, Min-Cian Chen, Ta-Hui Lin, Experimental study of the combustion characteristics of densified refuse derived fuel (RDF-5) produced from oil sludge, Original Research Article Fuel, Volume 116, 15 January 2014, Pages 201-207

The effects on auto-ignition of Petcoke mixtures with Refuse Derived Fuel

D. Bakirtzis, P. Danias, V. Tsapara, C. Michalopoulos and S. Liodakis

National Technical University of Athens School of Chemical Engineering
Laboratory of Inorganic and Analytical Chemistry, 9 Heroon Polytechniou Str, 15780 Athens
tel: +30210772316 Fax: +302107723377

E-mail: d.bakirtzis@hotmail.com

P3-40

For environmental and energy reasons petcoke is usually blended with refuse derived fuel (RDF) in order to be co-incinerated for use in the cement industries. The way that the RDF proportion in this binary system Petcoke/RDF affects auto-ignition incubation time of the blend has been studied. RDF as additive in these binary blend alters the kinetics of the system enhancing the quality of the flammable volatiles. Pyrolysis of the inner mass of the material produces volatiles, tars, carbonaceous char and mineral ash. The flammable gases emerging through the outer layer of the solid fuel, mixing with air in a boundary layer producing auto-ignition in conditions of adequate temperature and oxidative agent, in order the volatile-air mixture to reach a sufficiently high temperature, exceeding the flammability limits [1-3]. Therefore, auto-ignition requires a minimum supply volume of flammable gases derived from a minimum *pyrolysis rate*.[1] In this study the auto- ignition has been investigated employing a customized apparatus as depicted at Figure 1.

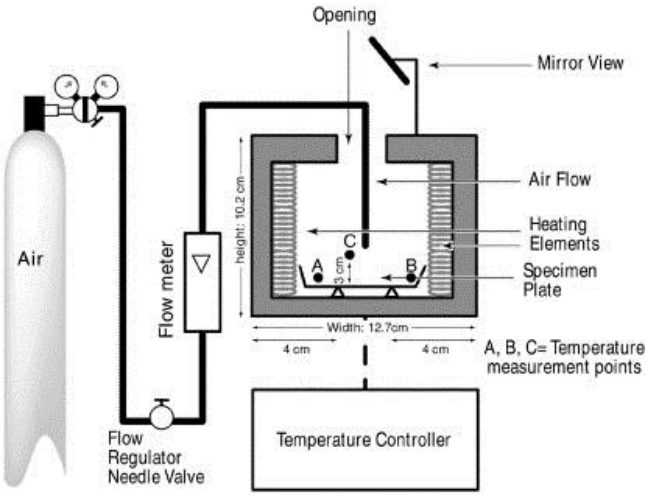


Fig. 1. Diagrammatic presentation of the apparatus used for measuring the spontaneous ignitability of petcoke blends with RDFspecies.

References

[1] S. Liodakis , D. Bakirtzis, E. Lois, D. Gakis The effect of (NH4)2HPO4 and (NH4)2SO4 on the spontaneous ignition properties of Pinus halepensis pine needles Laboratory of Inorganic and Analytical Chemistry, Department of Chemical Engineering, National Technical University of Athens (NTUA), 10 December 2001

[2] Wei-Qiang Han, Chun-De Yao M. de Joannon, A. Saponaro, A. Cavaliere, M. de Joannon, Research on high cetane and high octane number fuels and the mechanism for their common oxidation and auto-ignitionReview Article Fuel, Volume 150, 15 June 2015, Pages 29-40Proc. Combust. Inst. 28 (2) (2000) 1639–1646

[3] Dimitris J. Diamantis, Dimitris C. Kyritsis, Dimitris A. Goussis, The reactions supporting or opposing the development of explosive modes: Auto-ignition of a homogeneous methane/air mixtureOriginal Research Article Proceedings of the Combustion Institute, Volume 35, Issue 1, 2015, Pages 267-273

Assessment of the synergistic fire-retardant effect of a new gel-carbonate mineral mixture in a large-scale test

D. Bakirtzis[1], V. Tsapara[1], D. Vorisis[1], S. Liodakis[1] and P. Joseph[2]

[1] Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens (NTUA),9 Iroon Polytecniou Street, Athens 157 73, Greece
[2] Fire Dynamics and Materials Laboratory, The Institute for Fire Safety Engineering Research and Technology (FireSERT), School of the Built Environment, University of Ulster, Newtownabbey BT37 0QB, Co. Antrim,, Northern Ireland, UK

E-mail: d.bakirtzis@hotmail.com.

P3-41

The fire-retarding effectiveness of three chemicals i) sodium polyacrylate (gel), ii) a commercial mixture of the carbonate minerals, huntite-hydromagnesite (Securoc) and iii) DAP (diammonium phosphate), was assessed on wooden blocks of Pinus sylvestris L. The main objective of this work was to derive benefits from the intrinsic properties of the gel when used as a dispersion agent. Thus, it was combined with the carbonate minerals (Securoc), which otherwise are used as dry powders [1], and an improved application was achieved. DAP, having a prominent use as a fire retardant [2], was used for comparison. The effectiveness of the fire retardants on the combustion of wooden blocks was assessed in a large-scale test which closely simulated a real fire scenario in a residential construction. According to the mass residue criterion (Figure), incorporating a gel and a carbonate mineral led to an improved fire-retarding efficiency (synergy) for wooden materials.

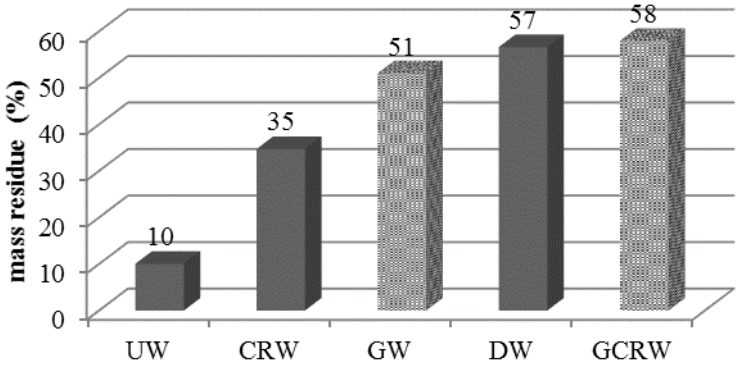


Figure 1 . Wooden block mass residue (%) before (UW) and after F.R. treatment (CRW: Securoc-treated wood, GW: gel-treated wood, DW: DAP-treated wood and GCRW: gel and Securoc-treated wood).

References

[1] S. Liodakis, V. Tsapara, I.P. Agiovlasitis and D. Vorisis, *Thermochim Acta*, 568 (2013) 156– 160.
[2] D. Bakirtzis, V. Tsapara, S. Liodakis and M. Delichatsios, *Thermochim Acta*, 550 (2012) 48– 52.

Thursday 24 September 2015

Royal Cruise Hall-A

Chair: O. Ataman, J. Stratis

Environmental Analysis

New matrix - free reference materials in the form of optical fibers for benzene and toluene analysis

M. Słomińska, P. Konieczka, J. Namieśnik

Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology,
G. Narutowicza 11/12, 80-233 Gdańsk, Poland

E-mail: korpala.m@poczta.onet.pl

Intensive development of analytical techniques for measurement of gaseous media and the negative effects of BTX (benzene, toluene, xylene) compounds make it particularly important to monitoring and determination of these compounds in the air. The problem is the availability of gaseous reference materials. Hence the need to seek new reference materials of volatile organic compounds, which will enrich the already existing trade offer on the market. The preparation of standard gas mixtures via thermal decomposition process (TD) is based on the controlled decomposition of surface compounds at a strictly defined temperature during the specified period of time. The individual stages of TD-based procedure for generating of standard gas mixtures are presented in Figure 1.

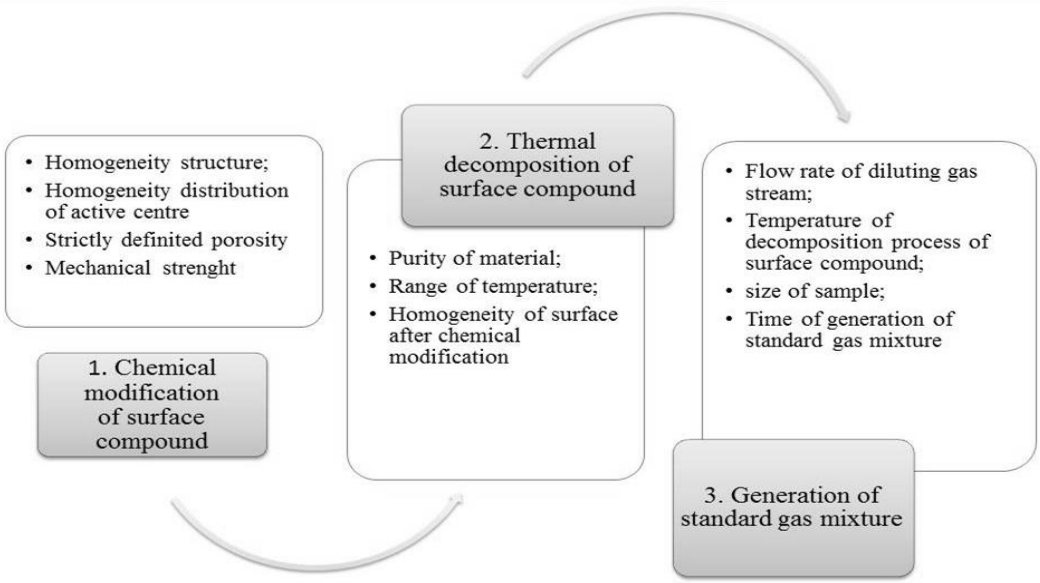


Fig. 1. Basic steps in the procedure for generating standard gas mixture with an application of TD process.

The results obtained at various stages of the research procedure (homogeneity, stability) confirmed the possibility of using prepared laboratory samples of materials as reference materials for benzene and toluene. For the prepared batch of materials reference values were determined.

Research stands an innovation way in the field of preparation of gaseous reference materials and its give a possibility to: simplify the calibration stage of apparatus, shorten the time of analysis, eliminate sources of error, obtain higher level of precision and accuracy of the analysis. Moreover, this form of reference materials provides a useful tool for routine screening in daily laboratory practice.

A Joint Research Project for the Production and Certification of Matrix Reference Materials for Environmental Analysis

A. Isleyen[1], J. Vogl[2], N. Scrundric[3], A. Jotanovic[4], T. Näykki[5], M. Horvat[6], A. Zoń[7], E. Bulska[8], M. Ochsenkühn-Petropoulou[9], S.Z. Can[1], M. Bilsel[1], K. Hafner[4], N. Perkola[5], B. Ari[1], M. Tunç[1], B. Binici[1]

[1]TÜBİTAK UME-National Metrology Institute-TURKEY
[2]BAM-Federal Institute for Materials Research and Testing-GERMANY
[3]DMDM- Directorate of Measures and Precious Metals-SERBIA
[4]IMBIH- Institute of Metrology-BOSNIA and HERZEGOVINA
[5]SYKE-Finnish Environment Institute-FINLAND
[6]IJS-Institute Jozef Stefan-SLOVENIA
[7]GUM-Central Office of Measures-POLAND
[8]UWAR-University of Warsaw-POLAND
[9]NTUA-National Technical University of Athens-GREECE

E-mail: alper.isleyen@tubitak.gov.tr

Reliable analysis of chemical indicators in water, sediment and soil samples for the purpose of environmental pollution assessment poses one of the greatest analytical challenges, having in mind the complexity of sample matrix and low concentrations of pollutants. Organics (pesticides, PAHs, PCBs, etc.) and heavy metals (Hg, Cd, Ni, Pb and As) represent target parameters. Laboratories performing sampling and tests in this field regulated by respective EU directives [1], need strong support in terms of providing them with appropriate matrix CRMs enabling the process of quality control. NMIs and DIs with proven metrological capabilities for the production and certification of such materials are necessary for the provision of quality data.

This project is aiming to develop capacity to produce CRMs for environmental analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on environmental CRM production in accordance with ISO Guide 34 [2]. Production process includes good manufacturing practices for processing materials, method development and validation for homogeneity, stability and characterisation tests, characterisation of selected analytes together with additional information about matrix constituents, the calculation of individual uncertainties (between units inhomogeneity, long term stability, characterisation) and combination of uncertainties to determine overall uncertainty of the matrix reference materials. Inter laboratory comparison registered as EURAMET project is set as the ultimate project outcome, confirming the partners' capabilities in applying newly acquired skills.

References

[1] Water Framework Directive 2008/105/EC – Annex II: Priority substances and other pollutants- http://ec.europa.eu/environment/water/water-framework/priority_substances.htm
[2] ISO Guide 34:2009 – General Requirements for the Competence of Reference Material Producers

Phase ratio variation approach to quantify adsorption behavior of volatile organic compounds in Nalophane sampling bags

J. Van Durme

KU Leuven - Technology Campus Ghent, Research Unit Molecular Odor Chemistry, Gebroeders De Smetstraat 1, 9000 Gent, Belgium

E-mail: jim.vandurme@kuleuven.be.

In the field of environmental analysis, researchers rely on the accurate qualitative and quantitative assessment of odorous compounds in the gas phase. In recent years, attention has been mainly given to advanced hyphenated analytical techniques and the development of new detectors (e.g. e-noses, SIFT-MS, etc.). However, the sample collection step is equally important and strongly influences reproducibility and accuracy. Whole air sampling using polymeric bags is still one of the most frequently used sample collection methods in the field. The degree of scalping, which is defined as sorption of the volatiles on the inner surface of polymeric sampling bag, is often underestimated, in particular in the field of environmental sampling (Figure 1).

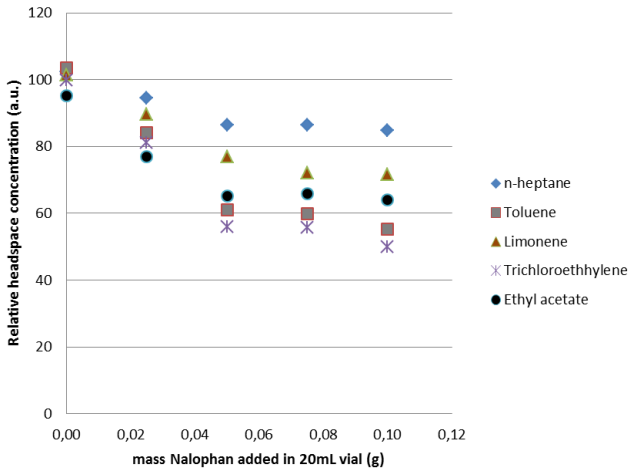


Fig. 1 Relative average headspace concentration (n=3) in function of introduced mass of Nalophan in 20 mL vial (darkness, T=25°C, RH = 70%) measured after 15 hours of incubation (all error bars were below 5% RSD)

In this work a Phase Ratio Variation (PRV) method is suggested as a fast and efficient manner for predicting the degree of scalping for individual compounds, and thus enabling to compensate for sorption phenomena. This method requires limited measurements, without the need for time-consuming calibrations. Moreover, a correlation was found between partitioning coefficients and the liquid molar volume for a number of aliphatic, aromatic and oxygenated compounds.

References

[1] J. Van Durme and B. Werbrouck, *Environ. Sci. Pollut. Res.*, Epub ahead of print, 2015.

PM_{10} emissions: the importance of biomass type and combustion conditions

A. Zosima and M. Ochsenkühn-Petropoulou

Laboratory of Inorganic and Analytical Chemistry, School of Chemical Engineering, National Technical University of Athens, Iroon Polytechniou 9, 15773, Athens, GR

zosang278@hotmail.com

TH04

Biomass is evolved to be a sustainable energy source, environmentally friendly fuel with potentials for replacing electricity and fossil fuels. However, wood combustion is considered as a source of ambient PM_{10} emissions and PAHs that have been associated with adverse health effects according to scientific studies [1]. The increasing need of biomass usage demands to study and evaluate the influences of combustion technology and fuel characteristics on air quality and human health. Wood biomass such as pellets and briquettes has also become more common, especially in Europe and Greece during the last years. Pellets are relatively new and are used in residential appliances such as stoves and boilers. Emissions from pellet combustion are related to fuel quality and combustion technology [2].

The aim of the present work was to investigate the impact of biomass combustion with respect to conditions and fuel types, on particle emissions (PM_{10}) and their carbonaceous, metals, anions and PAHs content. The maximum permitted particle emission limit is 150 mg/m^3. Special concern was given on sampling, quantification and characterization of PM using different appliances, fuels and operating procedures. For this purpose a lab scale sampling device was developed in order to burn the biomass and collect directly their particulate matter emissions in a filter holder system providing it with different flow oxygen (20 % and 13 % in the exhaust gas which simulate a combustion in an open fireplace and in pellet stoves, respectively) [3]. Moreover, the combustion took place under real conditions such of two pellets stoves (8,5 and 10 kW) and one open fireplace, where 8 fuel types of biomass were tested. Different analytical methods of leaching were applied for the quantitative determination of metals and anions. Instruments such as: inductively coupled plasma-optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), ion chromatography, total organic carbon analyzer (TOC-VCSH) and CHN elemental analyzer, were used for the quantitative analysis of PM_{10}. Furthermore, an analytical procedure was developed for the quantitative determination of 16 PAHs using liquid-liquid extraction and subsequent measurement by gas chromatography coupled to a mass spectrometer (GC-MS). Pellets originated from olive trees and from non mixture trees were found to emit the lowest particulate matter in relation to the others, so they are considered healthiest and suitable for domestic heating reasons. In general, the results show that biomass open burning is an important PM_{10} emission source.

References

[1] S. Ghafghazi, T. Sowlati, S. Sokhansanj, X. Bi and S. Melin, *Renew. Sust. Energ. Rev.*15 (2011) 3019-3028.
[2] G. Toscano, D. Duca, A. Amato and A. Pizzi, *Energy* 68 (2014) 644-650.
[3] A. Zosima and M. Ochsenkühn-Petropoulou, Fresen. Environ. Bull. 24 (2015) 146-156.

Decision Making in Sewage Sludge Management

M. Malioka, E. Darakas, A. Kungolos and D. Latinopoulos

Division of Hydraulics and Environmental Engineering, Dept. of Civil Engineering, Aristotle University of Thessaloniki, GR- 54124 Thessaloniki, Greece

E-mail: mmalioka@civil.auth.gr

The sludge management problem is mainly related to the continuous increase in sludge production, the high costs of sludge treatment and the risks sewage sludge may have to the environment and to human health [1]. Sludge management should be integrated into a new framework that takes into account environmental, technical, scientific, economic, legislative and social factors. It has been proved that a multi-criteria model for a case by case solution to the sludge management problem seems to be of great importance and interest [2].

Multi-criteria decision making (MCDM) or multi-criteria decision analysis (MCDA) is a broad term used to describe any decision where multiple and conflicting criteria have influence on the decision [3]. The choice of the appropriate decision-making methodology should comply, whenever possible, with the special characteristics of each problem. In environmental planning, a whole process is needed in order to conclude in a decision, which comprises all the criteria that should be taken into account [4]. In this paper, the categories of the methodologies of multi-criteria decision analysis are presented and the factors related with the selection of the appropriate methodology, as well.

A MCDA starts with the process of determining the envisioned objectives. It continues with the relationships between projects or alternatives, the impacts that a project can produce (in the environment, society and economy), the selection criteria and corresponding thresholds and goes on with the analysis of some techniques currently used to help the decision making [5]. In this paper, preliminary crucial aspects of the process related with sludge management are presented.

References

[1] W.H. Rulkens, Sustainable sludge management – what are the challenges for the future?, Water Science and Technology, Vol. 49 No 10 (2004) 11-19.
[2] M. Malioka, E. Darakas and A. Kungolos, Multicriteria Analysis in Sewage Sludge Management, 4th International Conference of Hellenic Solid Waste Management Association "Solid waste management in crisis: New challenges and prospects", 30th November – 1st December 2012 (2012).
[3] J. A. Scott, W. Ho, P. K. Dey, A review of multi-criteria decision-making methods for bioenergy systems, Energy, Vol. 42 (2012) 146-156.
[4] S. Bakopoulou, Wastewater reuse in irrigation: Evaluation of Economic, Social and Environmental parameters for sustainability assessment of advanced systems of Secondary Treated Effluents Energy, PhD Thesis, Department of Planning and Regional Development, University of Thessaly, (2009).
[5] Nolberto Munier, A strategy for using multicriteria analysis in decision – making, A guide for simple and complex environmental projects, Springer, ISBN 978-94-007-1511-0 (2011).

Influence of elevated pH and strong organic load presence on Granular Activated Carbon's bromate removal ability

F.A. Megalopoulos, M.T. Ochsenkühn-Petropoulou

National Technical University of Athens, School of Chemical Engineering, Inorganic and Analytical Chemistry Laboratory, Iroon Polytechneiou Str. 9, 157 80 Athens, Greece

E-mail: fmegalopoulos@texne.gr

TH06

Bio-fouling is one of the most critical problems that cooling circuit operators have to deal with. It can cause severe problems in heat exchanging as well as equipment destruction. One of the most common ways to disinfect cooling water is by brominating it. Bromination is specifically used when cooling water's pH is maintained above 8, in order to render it less corrosive.

The amount of bromine, in the form of hypobromous, to be added to achieve specific residual has been studied and reported[1]. However hypobromous decomposition can lead to the formation of BrO_3^-[2]. Bromate is a strong carcinogen to humans, and thus it's concentration in drinking water is regulated by US EPA as well as the EU to 10μg/L. Hypobromous decomposition is enhanced by sunlight and the presence of residual free chlorine as well as CuO[3] which a is material found in the construction of heat exchangers. Granular Activated Carbon (GAC) is one of the most widely used adsorbents in industry and is a material with proven capability to remove bromate from water. In this work GAC's ability to remove bromate from alkaline as well as organic load rich cooling water is investigated.

Cooling water was taken from a large metal processing industrial unit in the Greek territory and a dose of 2mg/L of BrO_3^- was added. Initially the pH was adjusted to 10 and then 12. Further on, the organic load of the aliquots was adjusted to 10 mg/L and 15 mg/L with the use of humic acid sodium salt. Isotherm curves were constructed using GAC type 1204W from Cabot Norit which has been found to possess superior bromate removal ability[4]. Residual bromate was measured after 48h contact time using Ion Chromatography (EPA Method 300.1).

The derived isotherm curves fit best the Freundlich model. Increasing pH gravely inhibits GAC's ability to remove bromate from cooling water. Increasing organic load content also inhibits bromate removal but in a less forceful manner.

References

[1] F.A. Megalopoulos, M.T. Ochsenkuehn-Petropoulou, Estimation of the residual bromine concentration after disinfection of cooling water by statistical evaluation. *J. Env. Sci. Heal A* 50 (2015) 144-150

[2]R.C. Beckwith, D.W. Margerum, Kinetics of hypobromous acid disproportionation. *Inorg. Chem.* 36 (1997) 3754-3760

[3] L. Chao, U. Von Gunten, J.P. Croue, Chlorination of bromide-containing waters: Enhanced bromate formation in the presence of synthetic metal oxides and deposits formed in drinking water distribution systems. *Wat. Res.* 47 (2013) 5307-5315

[4] F.A. Megalopoulos, M.T. Ochsenkuehn-Petropoulou, Bromate removal from Industrial Cooling Water with the Use of Granular Activated Carbon, IWA Balkan Young Water Professionals Conference, 10-12 May 2015, Thessaloniki GR, Conference Proceedings pp.420-424

Optimizing magnetic nanoparticles for drinking water technology: The case of Cr(VI)

E. Kaprara[1], M. Mitrakas[1], N. Andritsos[2], K. Simeonidis[2]

[1]Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece
[2]Department of Mechanical Engineering, University of Thessaly, Volos, Greece

E-mail: kaprara@auth.gr

The possibility to incorporate nanotechnology in environmental applications has been widely examined during the last years as a way to improve the efficiency of conventional treatment methods. The aim of this study is to provide important information about the possibility to apply magnetite nanoparticles in water treatment technology for Cr(VI) removal with respect to the economic and environmental impact. Magnetite nanoparticles were prepared at kilogram-scale by the aqueous co-precipitation of Fe^{2+} and Fe^{3+} salts under alkaline conditions in a two-stage continuous flow reactor. The mean particle diameter varies depending on the iron salt precursor; precipitation of iron chlorides results in nanoparticles with a size of 10 nm whereas the particle diameter increases to about 20 nm with the use of iron sulfates and may reach 30 nm with Mohr's salt.

The removal efficiency of magnetite nanoparticles for Cr(VI) was studied in batch adsorption experiments at equilibrium pH 5-8. Magnetite nanoparticles prepared by iron sulfates and the Mohr's salt (q_{50}=5.5 μg/mg) show a significantly higher efficiency than those precipitated by iron chlorides (q_{50}=4.3 μg/mg) indicating the direct correlation between the Fe^{2+}/Fe^{3+} ratio in iron oxide and the Cr(VI) removal yield. The removal ability of Fe_3O_4 nanoparticles is significantly high at acidic environment while their performance is inhibited above pH 7. For instance, the q_{50}-value meets a maximum of around 4 μg/mg when experiment was performed at pH 5 but decreases to just above 1 μg/mg at pH 8.

X-ray Photoelectron Spectroscopy (XPS) was applied to identify the mechanism of chromate uptake from magnetite nanoparticles. The reduction of Cr(VI) by the Fe^{2+} sites of Fe_3O_4 nanoparticles is the dominating mechanism of chromium uptake. Formed Cr(III) species precipitate as an insoluble hydroxide on particles surface rather than substitute iron sites in magnetite's structure and participate in mixed oxides. However, a significant percentage of Cr(VI) species was detected when experiments were performed at pH values below 6 when the efficiency of Cr(VI) removal increases.

The successful operation of a small-scale system consisting of a contact reactor and a magnetic separator demonstrates a way for the practical introduction and recovery of magnetite nanoparticles in water treatment technology.

References

[1] K. Simeonidis, E. Kaprara, T. Samaras, M. Angelakeris, N. Pliatsikas, G. Vourlias, M. Mitrakas, N Andritsos, *Sci. Tot. Environ.*, 535 (2015) 61-68.

Thursday 24 September 2015

Royal Cruise Hall-A

Chair: A. Bobrowski, F. Tsopelas

Electrochemistry 2

Non-traditional electrode materials for voltammetric and amperometric monitoring of biologically active organic compounds

J. Barek[1], J. Fischer[1] and J. Wang[2]

[1]Charles University in Prague, Faculty of Science, University Research Centre UNCE "Supramolecular Chemistry", Department of Analytical Chemistry, UNESCO Laboratory of Environmental Electrochemistry, Albertov 6, CZ-128 43 Prague, Czech Republic.
[2]University of California San Diego (UCSD), La Jolla, Department of Nanoengineering, 9500 Gilman Drive 0448, CA 92093-0448, USA.

E-mail: barek@natur.cuni.cz; josephwang@eng.ucsd.edu

Modern voltammetric and amperometric techniques can play important role in monitoring of submicromolar concentrations of various biologically active organic compounds. The general tendency to substitute mercury has lead us to extensive investigation of the use of various silver amalgam electrodes [1] for determination of electrochemically reducible pesticides, ecotoxic nitrophenols, antitumor drugs and biomarkers of exposure to genotoxic compounds in various environmental and biological matrices. It will be shown that these electrodes can be used down to subimcromolar concentrations and in combination with a preliminary separation and pre-concentration using solid phase extraction even to nanomolar concentrations both in environmental (e.g. surface waters) and biological (e.g. urine) matrices. The same holds for the use of newly developed bismuth film electrodes [2,3] previously used mainly for inorganic compounds. Our recent results of their successful application for determination of trace amounts of electrochemically reducible substances will be presented. For electrochemically oxidisable organic compounds we have the best experience with the application of boron doped diamond film electrodes [4] with extremely broad potential window, low noise, and high resistance to passivation, which is probably the biggest problem for practical applications of solid electrodes in trace analysis of biologically active compounds in complex matrices. Recent application of above mentioned non-traditional electrode materials in trace environmental a biomedical analysis both in batch and in flow arrangement (wall-jet, thin-layer, etc.) will be presented and outlooks for their further development and improvement will be discussed.

Acknowledgement

Financial support from Czech Ministry of Education, Youth and Sports (project LH 13002 Program KONTAKT II) is gratefully acknowledged.

References

[1] A. Danhel, J. Barek, *Current. Organic Chemistry* 15 (2011) 2957-2969.
[2] N. Serrano, A. Alberich, J.M. Diaz-Cruz, C. Arino, M. Esteban, *TrAC, Trends in Analytical Chemistry*, 46 (2013) 15-29.
[3] J. Wang, Electroanalysis, Electroanalysis, 17 (2005) 1341-1346.
[4] J. Svitkova, T. Ignat, L. Svorc, J. Labuda, J.Barek, *Critical Reviews in Analytical Chemistry*, submitted.

A new electrochemical approach for determination of antihypertensives in pharmaceuticals and biological samples based on boron-doped diamond sensor

K. Cinková and Ľ. Švorc

Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, Bratislava, SK-812 37, Slovak Republic

kristina.cinkova@stuba.sk

TH09

Amlodipine represents a third generation and long-acting 1,4-dihydropyridine derivative, which is currently the most frequently used drug for hypertensive patients. Concerning its adverse effects after ingestion, some risk factors increase the likelihood of peripheral edema, palpitations and nausea[1]. Therefore, pharmaceuticals containing amlodipine have to undergo a strict quality control, which requires the development of simple, rapid and reliable analytical methods for the detection and quantification of this drug in both pharmaceuticals and biological samples. Recently, the effort of electrochemists in drug analysis has been focused on the utilization of perspective electrode materials. Herein, we present the novel approach for the electrochemical determination of amlodipine using boron-doped diamond electrode. Cyclic voltammetric studies indicated that the oxidation of amlodipine is irreversible with single and well-shaped peak at a potential of +0.75 V (*vs.* Ag/AgCl/3 M KCl electrode) in Britton-Robinson buffer solution at pH 5. The electrode reaction of amlodipine on boron-doped diamond electrode was shown to be a two-electron diffusion-controlled process. Under optimized conditions and using differential pulse voltammetry, the current response of amlodipine was proportional in a concentration range of 0.2-38 μM with two linear segments from 0.2 to 6 μM (R^2 = 0.996) and from 6 to 38 μM (R^2 = 0.998), respectively, with a limit of detection of 0.07 μM (28.6 μg L^{-1}) and a good repeatability (relative standard deviation of 3.6 % at 9.9 μM for n = 20). The method was successfully applied to the determination of amlodipine in pharmaceutical tablets without any interference and with result similar to that declared by the producer. Additionally, a biological relevance of the developed procedure was demonstrated by analysis of model human urine samples with adequate recoveries. The interference study revealed that the use of proposed method in this kind of analysis could be limited depending on the presence of particular excess of some common urinary compounds (uric acid, dopamine, ascorbic acid and glucose). The proposed methodology with boron-doped diamond electrode represents an effective and alternative tool instead of commonly used glassy carbon and chemically-modified electrodes for electrochemical determination of amlodipine.

Acknowledgements

This work has been supported by the Grant Agency of the Slovak Republic (grant No. 1/0051/13).

References

[1] B. Streel, C. Zimmer and R. Sibenaler, *J. Biochem. Bioph. Meth.*, 54 (2002) 357-368.

New method for glass electrode internal calibration in the determination of functional groups of humic substances

I. Boal-Palheiros

Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

E-mail: isabel.boal@ua.pt

In most aquatic environments there is a great variety of dissolved organic compounds rich in anionic functional groups (e.g. phenolic compounds, humic and fulvic acids) which are able to form various complexes on inorganic particles present in surface waters and soils and also coat the surface of mineral particles. The presence of these natural complexants such as humic and fulvic acids modifies and extensively influences particle interactions and consequently soil erosion, particle transport, sediment formation, and also, due to their ability to bind metal ions, the fate of pollutants, particularly heavy metal ions in the environment [1].

The ionization of the functional groups of humic substances determines their charge and consequently their binding behavior This has tremendous consequences in particle coating and ion complexation and, in consequence, in the geochemical cycling of macro and micro nutrients as well as controlling the free concentration of toxic compounds and metal ions. The extent of ionization depends on media composition but pH is undoubtedly the single most important variable. The characterization of humic substances functional groups may be achieved from base titrations. These are rapid, simple, and affordable procedures, but not very accurate for the determination of weaker acidic groups, such as phenolic ones mainly due to the alkaline error of glass electrode [2].

An entirely new approach to obtain equilibrium constants from acid-base titrations is proposed in this work. In this procedure the electrode parameters and the protonation constants are determined from within the sample solution titration itself. The method's main feature is to use *a priori* information on the sample solution to perform full parameter extraction using data from the strongly acidic and the strongly alkaline regions, through non linear regression analysis. It was applied to two different types of titrations, strong acid and fulvic acid, followed by two electrodes. Results yielded by the two electrodes agreed rather closely within the 2.5-11.5 pH range. They also proved to be stable when a more refined model that fits the titrated solution in the total pH range, using the full data set, was applied. A comparison with traditional methods was also undertaken and demonstrated that the novel approach yields more precise and reliable results, especially in the extreme lower and upper pH values. From titration data full characterization of both strongly and weakly acidic functional groups of humic substances was successfully attained. This method may have a wide use in the study of protonation equilibria due to its high accuracy and reproducibility but was shown to be particularly useful when dealing with complex substances of ill defined composition such as humic substances.

References

[1] J. Buffle, Complexation Reactions in Aquatic Systems, Ellis Horwood, Chichester, 1988

[2] C.J. Milne, D.G. Kinniburgh, E. Tipping, *Environ. Sci. Technol.*, 35 (2001) 2049-2059

Derivative spectroscopic determination of enrofloxacin in some natural samples

Ch.M. Rashid[1], N.A. Fakhre[1] and U.K. Ahmed[2]

[1]Dept. of Chemistry, College of Education, Salahaddin University-Erbil, Iraq
[2]Program Head of MSc. Forensic Science Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia

E-mail: havras@yahoo.com

TH11

Enrofloxacin is the first specified Fluoroquinolones developed for veterinary application, which belongs to the second generation of quinolone antibiotics fluorinated in position 6 and bearing a piperazinyl moiety in position 7. Similar to other Fluoroquinolones, Enrofloxacin is used in the treatment of systemic infections including urinary tract, respiratory, gastrointestinal, and skin infections. Because of a very broad spectrum of activities against both Gram-negative and Gram-positive bacteria and lower side effects, Enrofloxacin has also been widely used for the treatment of some infectious diseases in pets and livestock. However, Enrofloxacin residues may persist in animal body and may result in the development of drug-resistant bacterial strains or allergies [1]. A new, simple, rapid, wide applicable range and reliable derivative spectrophotometric method has been developed for determination of enrofloxacin.

References

[1] Z. Hai-tang, J. Jin-qing, W. Zi-liang, C. Xin-yao, L. Xing-you, W. San-hu, Z. Kun, C. Jin-shan, *Journal of Zhejiang University-SCIENCE B (Biomedicine & Biotechnology* ,12 (2011) 884-891

A novel respirometer for determination of compost stability

C. Tsiodra and A.G. Vlyssides

National Technical University of Athens, School of Chemical Engineering, Laboratory of Organic Chemical Technology Iroon Polytechniou 9, Zografou 15780, Athens,

E-mail: avlys@tee.gr

Composting is an aerobic biological process of organic substrates stabilization with low moisture content (up 50%). During the composting process the biological activity of the organic substrates depends on the residual biodegradable substrate content as well as the quantity and quality variety of the microbial cultures. The oxygen uptake rate (mass of oxygen per unit of biomass weight and per unit of time) could be characterized the indirect monitoring parameter of the biological process progress. The measurement of this parameter is performed with devices called respirometry. These devices calculate the oxygen uptake rate using the total CO_2 production measurements in a batch bioreactor where an amount of composting material and oxygen are enclosed for enough time under controlled temperature. The result from these devices represents the mean value of oxygen uptake rate but not the maximum oxygen uptake that is a more important parameter for the estimation of biological activity [1].

In this work a novel respirometer is presented which can measure the maximum oxygen uptake rate of an organic substrate and the time that the autotrophic and heterotrophic bioreactions are completed. With these results someone could be estimate the status of a composting process. Specifically in this device consist from a closed bioreactor where 150 gr of solid organic substrate are putting and an air volume of 150 l is recirculating continuously through the solid mass by a peristaltic pump with a flow rate of seven liter per hour. The temperature and moisture of the organic substrate is under control and the measurements oxygen and CO_2 content in the recirculating air are collected continuously. Loading these measurements in a proper computer program, the maximum oxygen uptake rate and the time of bioreactions overcome are calculated. Stabilization of the gas concentrations completed approximately 12 to 48 hours depending on the temperature. The current process has been tested on different substrates. The characteristic oxygen absorption curves which were obtained are correlated with other parameters such as Water Holding Capacity (WCH), pH, EC, Humic and Fulvic contents as well as Cation Exchange Capacity (CEC). It is observed that there is good correlation with the measured oxygen consumption in order to be used for the prediction of compost evolution of any substrate. As the composting time is being the maximum oxygen uptake rate and the stabilization time are reduced (see figure 1).

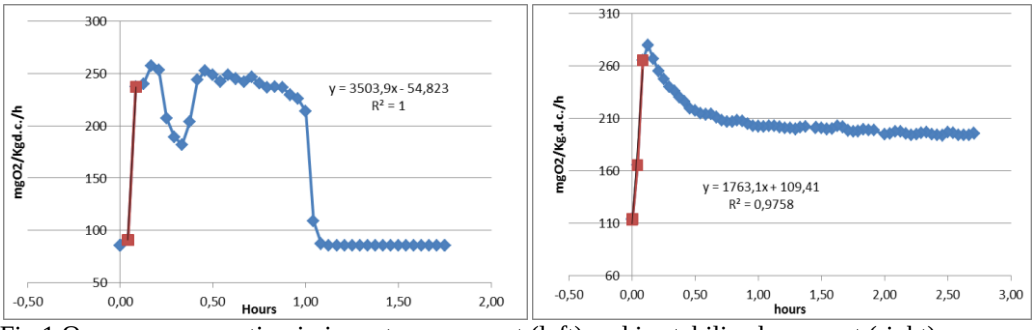


Fig.1 Oxygen consumption in immature compost (left) and in stabilized compost (right).

References

[1] R.G.Gómez, F.G. Lima and A.S.Ferrer, The use of respiration indices in the composting process: a review, *Waste Management & Research*, 24 (2006) 37-47.

Index of authors

Sponsors

ASTERIADIS

ANTISEL
A. SELIDIS BROS SA

ELSEVIER

Authorized Distributor
PerkinElmer
For the Better

RIGAS LABS
When details lead to excellence.....

Interlab
Κωνσταντίνος Οικονόμου
Διεθνής Εργαστηριακός Εξοπλισμός Ε.Π.Ε.

HELLAMCO
SCIENTIFIC EQUIPMENT

BIOLAB

KONSTANTOPOULOS S.A.
FOOD INDUSTRY SINCE 1956

ATHENIAN BREWERY
AMSTEL Heineken open your world ΑΛΦΑ

INOMESSINIAKI
Winery

Vis olivae

IMA-2015