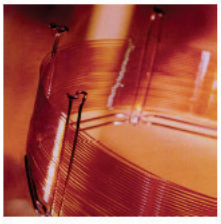
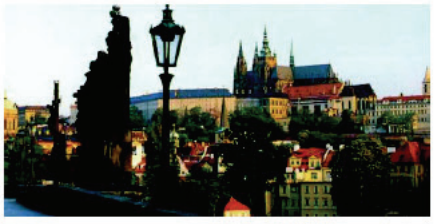
BOOK OF ABSTRACTS

1st European Workshop on AMBIENT MASS SPECTROMETRY AND RELATED MASS SPECTROMETRY-BASED TECHNIQUES IN FOOD / NATURAL PRODUCTS CONTROL: Safety, Authenticity, Forensics, Metabolomics

June 18–20, 2012
Prague, Czech Republic

Jana Pulkrabová, Monika Tomaniová, Michel Nielen, Jana Hajšlová
Editors


INSTITUTE OF CHEMICAL TECHNOLOGY PRAGUE

RIKILT WAGENINGEN UR

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June 18–20, 2012 • Prague • Czech Republic

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RIKILT - Institute of Food Safety, Wageningen University, The Netherlands

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WORKSHOP PROGRAM

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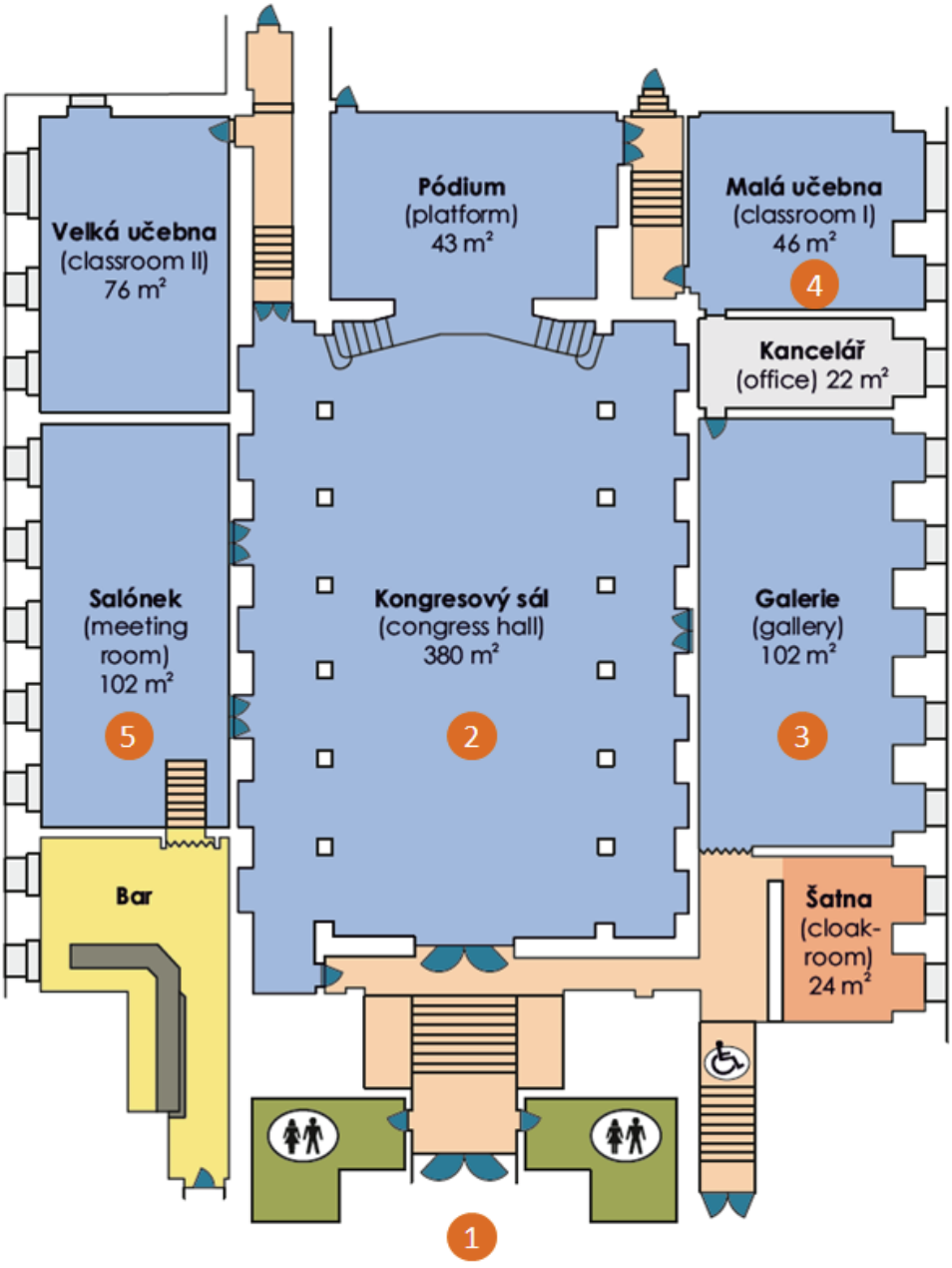
PLAN OF THE MASARYK COLLEGE CONFERENCE CENTRE



1:	Entrance to the conference centre & Registration desk
2:	Workshop hall & Poster area Exhibition area Vendor workshop room I
3:	Vendor workshop room II
4:	Vendor workshop room III
5:	Catering area (coffee breaks, lunches, Welcome Get Together Party)

RAFA AMS workshop – PROGRAM AT A GLANCE

Time / Date	MONDAY June 18, 2012	TUESDAY June 19, 2012	WEDNESDAY June 20, 2012
9:00–10:00		Oral session 4 Applications in Food Authenticity	Oral session 6 General Strategies in Data Handling and Interpretation in Mass Spectrometry-Based Metabolomics
10:00–10:30	**Registration** for the workshop Masaryk College Conference Centre		
10:30–11:00		Coffee break / Exhibition	Brunch / Exhibition
11:00–12:00		Vendor workshops Part I	Vendor workshops Part III
12:00–13:00		Vendor workshops Part II	Final discussion panel Advantages and Limitations of Ambient Mass Spectrometry Future Perspectives of Ambient Mass Spectrometry
13:00–13:30	Opening of the workshop	Lunch / Exhibition	
13:30–14:00	Oral session 1 Basic Principles of Most Widely Used Ambient Mass Spectrometry Techniques: Instrumentation and Fundamentals		Closure of the workshop
14:00–14:30		Poster session / Exhibition	
14:30–15:00			
15:00–15:30	Coffee break / Exhibition	Coffee break / Exhibition	
15:30–17:30	Oral session 2 Applications in Food Safety	Oral session 5 Applications in Metabolomics	
17:30–18:30	Oral session 3 Applications in Forensic Analysis	LAB Tour Department of Food Analysis and Nutrition, ICT Prague	
18:30–19:30	Welcome Drink Masaryk College Conference Centre		
20:00–22:30		Get Together Dinner Slavia restaurant (Prague downtown)	

MONDAY, June 18, 2012

10:00–13:00 **Registration for RAFA AMS workshop**

Masaryk College Conference Centre

13:00–13:30
Conference hall

OPENING of the workshop

Welcome to RAFA associated workshop

***Jana Hajslova**, chairwoman of RAFA AMS workshop, Institute of Chemical Technology, Prague, Czech Republic*

***Michel Nielen**, co-chairman of RAFA AMS workshop, RIKILT–Institute of Food Safety, The Netherlands*

History of Ambient Mass Spectrometry

***Jana Hajslova**, Institute of Chemical Technology, Prague, Czech Republic*

13:30–15:00
Conference hall

ORAL SESSION 1: Basic Principles of Most Widely Used Ambient Mass Spectrometry Techniques: Instrumentation and Fundamentals

13:30–13:50 L1

DART - INSTRUMENTATION, APPLICATIONS AND FUNDAMENTALS

***Facundo Fernandez**, Georgia Institute of Technology, Atlanta, Georgia, USA*

13:50–14:10 L2

ATMOSPHERIC PRESSURE SOLIDS ANALYSIS PROBE (ASAP) - INSTRUMENTATION AND FUNDAMENTALS

***Malcolm Driffield,** The Food and Environment Research Agency, York, UK*

14:10–14:30 L3

INTRODUCTION TO DESI MASS SPECTROMETRY

***Michel Nielen,** RIKILT–Institute of Food Safety, Wageninegn, The Netherlands*

14:30–14:50 L4

LIQUID EXTRACTION SURFACE ANALYSIS (LESA): BASIC PRINCIPLE AND REVIEW OF RECENTLY PUBLISHED STUDIES

***Andreas Wiesner,** Advion, Harlow, UK*

15:00–15:30 **Coffee Break / EXHIBITION**

15:30–17:30
Conference hall

ORAL SESSION 2: Applications in Food Safety

15:30–16:00 L5

DART-TOF-MS: A TIME-SAVER IN ANALYTICAL CHEMISTRY

***Christian Klampfl**, Johannes Kepler University, Linz, Austria*

16:00–16:30 L6

THE USE OF HIGH RESOLUTION MASS SPECTROMETRY (SYNAPT G2 HDMS) WITH ASAP SAMPLE INTRODUCTION FOR THE ANALYSIS OF PLASTICISERS IN THE GASKETS OF FOOD JAR LIDS

***Malcolm Driffield,** The Food and Environment Research Agency, York, UK*

16:30–17:00 L7

HPTLC-DART-MS FOR FOOD SAFETY AND NATURAL PRODUCTS CONTROL

***Gertrud Morlock,** University of Hohenheim, Stuttgart, Germany*

17:00–17:30 L8

DART-MS AS A TOOL FOR MYCOTOXINS SCREENING

***Milena Zachariasova,** Institute of Chemical Technology, Prague, Czech Republic*

17:30–18:30 Conference hall		**ORAL SESSION 3:** **Applications in Forensic Analysis**
17:30–17:50	**L9**	**INTRODUCTION TO FOOD FORENSICS** ***Michel Nielen,*** *RIKILT–Institute of Food Safety, Wageninegn, The Netherlands*
17:50–18:20	**L10**	**INVESTIGATION OF HORMONES IN TISSUES USING IMAGING DESI-MS** ***Eva de Rijke,*** *RIKILT–Institute of Food Safety, Wageninegn, The Netherlands*
18:30–19:30		**Welcome Drink** **(Masaryk College Conference Centre)**

TUESDAY, June19, 2011

9:00–10:30 Conference hall — **ORAL SESSION 4: Applications in Food Authenticity**

9:00–9:30 L11 — **APPLICATION OF DART-TOFMS IN CHICKEN FEEDING HISTORY**
Tomas Cajka, *Institute of Chemical Technology, Prague, Czech Republic*

9:30–10:00 L12 — **AUTHENTICATION OF FOOD AND FEED LIPIDS**
Jana Hajslova, *Institute of Chemical Technology, Prague, Czech Republic*

10:00–10:30 L13 — **UTILIZATION OF AMBIENT MASS SPECTROSCOPY TECHNIQUES TO AID IN BOTANICAL AUTHENTICATION**
Troy Smillie, *National Center for Natural Products Research, Research Institute of Pharmaceutical Sciences, Oxford MS, USA*

10:30–11:00 — **Coffee Break / EXHIBITION**

11:00–12:00 — **VENDOR WORKSHOPS: Part I**

Innovations in Direct MS/MS and LC-MS/MS Technology for Screening, Identification and Quantitation of Food Contaminants

AB SCIEX

Progress report: DART-MS for Rapid Food Characterization

ionSense®
Your source for open-air mass spectrometry

Waters' Universal Ion Source Architecture - ASAP & APGC

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12:00–13:00 — **VENDOR WORKSHOPS: Part II**

Ambient MS using the Ionsense DART and ID-Cube with Agilent's Portfolio of Mass Spectrometers

Agilent Technologies

New Solutions for High Throughput Food Screening Using DART-Orbitrap Technology

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific

13:00–14:00 — **Lunch / EXHIBITION**

14:00–15:00 Conference hall — **POSTER SESSION / EXHIBITION**

15:00–15:30		**Coffee break / EXHIBITION**
15:30–17:35 Conference hall		**ORAL SESSION 5: Applications in Metabolomics**
15:30–15:55	**L14**	**UHPLC–MS AND DART-MS TECHNIQUES AS TOOLS FOR METABOLOMICS-BASED SCREENING OF ABIOTIC PLANT STRESS** ***Lukas Vaclavik,*** *Institute of Chemical Technology, Prague, Czech Republic*
15:55–16:20	**L15**	**THE POTENTIAL OF LC-HRMS METABOLOMICS FINGERPRINTING IN FOOD ANALYSIS: APPLICATION TO THE CONTROL OF FORBIDDEN SUBSTANCES** ***Gaud Dervilly-Pinel,*** *LABERCA, Nantes, France*
16:20–16:45	**L16**	**PROBING PLANTS BY DESI AND DART-MS: PROS AND CONS** ***Teris van Beek,*** *Wageningen University, The Netherlands*
16:45–17:10	**L17**	**PROBING CHEMICAL DIVERSITY OF BACTERIA BY LESA** ***Ales Svatos,*** *MPI for Chemical Ecology, Jena, Germany*
17:10–17:35	**L18**	**CHEMOMETRICS AND DIRECT INJECTION ANALYSIS OF VOLATILE COMPOUNDS BY PTR-TOF-MS: A TOOL FOR METABOLOMIC INVESTIGATIONS** ***Franco Biasioli,*** *Fondazione Edmund Mach, San Michele a/A, Italy*
17:35–18:30		**LAB TOUR** *at the* ***Department of Food Analysis and Nutrition, Institute of Chemical Technology, Prague,*** *Czech Republic*
From 20:00		**Get Together Dinner (Slavia restaurant, Prague downtown)**

WEDNESDAY, June 20, 2012

9:00–10:30 Conference hall

ORAL SESSION 6:
General Strategies in Data Handling and Interpretation in Mass Spectrometry-Based Metabolomics

9:00–10:30 **L19**

GENERAL STRATEGIES IN DATA HANDLING AND INTERPRETATION IN MASS SPECTROMETRY-BASED METABOLOMICS

INTRODUCTION TO CHEMOMETRIC APPROACHES

CASE STUDIES

Tomas Cajka, *Institute of Chemical Technology, Prague, Czech Republic*

10:30–11:00 **Brunch / EXHIBITION**

11:00–12:00 **VENDOR WORKSHOPS: Part III**

Liquid Extraction Surface Analysis (LESA), innovative upgrade technology for the TriVersa NanoMate®

Advion

GCxGC-TOF MS and ultra high resolution TOF MS with folded flight path (FFP TM) technology in food-related applications

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12:00–13:30 Conference hall

FINAL DISCUSSION PANEL:
Advantages and Limitations of Ambient Mass Spectrometry
Future Perspectives of Ambient Mass Spectrometry

RESEARCH INITIATIVES OF INDUSTRY vs. EXPECTATIONS OF END-USERS

13:30–13:45 Conference hall

CLOSURE OF THE WORKSHOP

POSTER SESSION

TUESDAY, June 19, 2012

14:00–15:00 POSTER SESSION

P-1 **A NEW TECHNOLOGY DUAL-SBSE-ATD-GC-MS-AMDIS FOR THE STUDY OF THE ENOMETABOLOME OF GRACIANO VITIS VINIFERA VARIETY**
Maria Arbulu, M. Carmen Sampedro, Alberto Gómez, M. Aránzazu Goicolea, Ramón J. Barrio

P-2 **CAPILLARY ELECTROPHORESIS COUPLED TO MASS SPECTROMETRY FOR THE RAPID EVALUATION OF MARKERS OF FOOD PRODUCTS AND FOOD PROCESSING**
Antonella Cavazza, Claudio Corradini, Chiara Bignardi

P-3 **ASSESSMENT OF FRUIT JUICE AUTHENTICITY USING UPLC/QTOF MS AND MARKERLYNX DATA EVALUATION**
Zora Jandrić, Aiman Abrahim, Nasir Rathor, Andrew Cannavan

P-4 **CHANGE OF FLAVONOIDS AS THE DEFENSIVE SUBSTANCE FOR CITRUS FRUIT PEEL AGAINST PENICILLIUM DIGITATUM USING LC-MS/MS: THEIR CONTRIBUTION TO OVERALL ANTIOXIDANT**
Hae Gyeong Kim, Mee Sung Lee, Do Yeon Kim, Jong Wook Kim, Jong Sung Jin, Sung Chul Shin

P-5 **DIRECT MS-ANALYSIS OF RADIX ANGELICAE SPECIES USING A NEW DIRECT INLET PROBE (DIP)-APCI ION SOURCE**
Sonja Krieger, Oliver J. Schmitz

P-6 **RAPID DETERMINATION OF THE MAIN PHYTOSTEROLS IN RED WINE BY UPLC-MS USING ATMOSPHERIC PRESSURE CHEMICAL INTERFACE**
Laura Millán, M. Carmen Sampedro, Nora Unceta, M. Aranzazu Goicolea, Ramón J. Barrio

P-7 **MULTICLASS DETERMINATION OF VETERINARY DRUGS RESIDUES IN ANIMAL PRODUCTS USING LC-MS/MS**
Luca Pellegrino, Enrico Parizia, Livio Tallone, Valeria Merlo

P-8 **STATINS AS ENVIRONMENTAL POLLUTANS IN WASTEWATER TREATMENT PLANT EFFLUENT IN NORTH SARDINIA**
Nicola Rubattu, Maria Cecilia Testa

P-9 **ANALYSIS OF MYCOTOXINS IN BARLEY USING UHPLC-HRMS: COMPARISON OF EFFICIENCY AND EFFICACY OF DIFFERENT EXTRACTION PROCEDURES.**
Josep Rubert, Zbynek Dzuman, Marta Vaclavikova, Milena Zachariasova, Jana Hajslova, Carla Soler

P-10 **OPTIMIZATION OF HEADSPACE IN-TUBE EXTRACTION GAS-CHROMATOGRAPHY MASS SPECTROMETRY METHOD FOR THE ANALYSIS OF SEA BUCKTHORN VOLATILE PROFILE**
Sonia Socaci, Maria Tofana, Carmen Socaciu, Liana Salanta, Adela Pintea

P-11 **DETECTION OF MYCOTOXINS AND ITS METABOLITES IN HUMAN MILK USING ORBITRAP TECHNOLOGY**
Carla Soler, Josep Rubert, Nuria Leon, Jose Miguel Soriano, Vicent Yusa, Jordi Mañes

P-12 **TRACING THE GEOGRAPHICAL ORIGIN OF AUSTRALIAN, CANADIAN, USA AND JAPANESE WHEAT FLOUR USING STABLE CARBON, NITROGEN AND OXYGEN ISOTOPE ANALYSIS**
Yaeko Suzuki, Eri Inoue, Rumiko Nakashita

P-13 **STUDY OF FATTY ACID PROFILES IN THREE NATIVE OLIVE CULTIVARS FROM ALBANIA**
Dritan Topi, Ana Paula Carvalho, Ana Maria Gomes

P-14 **ESI-LC-MS/MS METABOLIC PROFILING OF PHENOLIC ACIDS IN URINE OF HUMAN VOLUNTEERS AFTER CONSUMPTION OF LONICERA CAERULEA FRUIT**
Martina Zatloukalová, Jan Vacek, Pavel Kosina, Jitka Ulrichová, Vilím Šimánek

P-15 **CHARACTERIZATION OF NATURAL PRODUCTS WITH A MODIFIED AMBIENT SOURCE USING A MESH SCREEN SAMPLING CARD**
Jerry Zweigenbaum[1*]

P-16 **USING OF DART-MS TECHNIQUE FOR STUDY OF COD LIVER OIL SUPPLEMENT STABILITY**
Hana Novotna, Vera Schulzova, Jana Hajslova

P-17 **METABOLOMIC FINGERPRINTING/PROFILING EMPLOYING DART COUPLED WITH TOF-MS AND ORBITRAP-MS FOR DGGS AUTHENTICITY AND TRACEABILITY**
Hana Novotna, Tomas Cajka, Monika Tomaniova, Jana Hajslova

P-18 **AMBIENT MASS SPECTROMETRY AS A NEW TOOL FOR THE CHARACTERIZATION OF LIPIDIC FRACTION OF DIFFERENT KINDS OF FISH**
Vojtech Hrbek, Veronika Havelkova, Jana Pulkrabova, Lukas Vaclavik, Jana Hajslova

P-19 **MYCOTOXINS IN FOOD SUPPLEMENTS**
Zdenka Veprikova, Milena Zachariasova, Zbynek Dzuman, Marta Vaclavikova, Jana Hajslova

P-20 **QUANTITATIVE ANALYSIS OF CARBENDAZIM AND OTHER PESTICIDES IN FRUIT JUICES BY DIRECT ANALYSIS IN REAL TIME (DART) MASS SPECTROMETRY**
Elizabeth Crawford, Brian Musselman

CONTENT

VENDOR SEMINARS

JUNE 19, 2012 (11:00–12:00)

AB SCIEX – VENDOR WORKSHOP: INNOVATIONS IN DIRECT MS/MS AND LC-MS/MS TECHNOLOGY FOR SCREENING, IDENTIFICATION AND QUANTITATION OF FOOD CONTAMINANTS

INNOVATIONS IN DIRECT MS/MS AND LC-MS/MS TECHNOLOGY FOR SCREENING, IDENTIFICATION AND QUANTITATION OF FOOD CONTAMINANTS

Andre Schreiber

AB SCIEX, Canada

The presentation will cover ambient ionization techniques and differential mobility separation in conjunction with AB SCIEX LC-MS/MS systems. QTRAP and TripleTOF systems were used for confirmatory analysis using the power of MS/MS library searching and accurate mass MS/MS data.

JUNE 19, 2012 (11:00–12:00)

ION SENSE – VENDOR WORKSHOP: PROGRESS REPORT: DART-MS FOR RAPID FOOD CHARACTERIZATION

ID-CUBE DIRECT ANALYSIS IN REAL TIME HIGH-RESOLUTION MASS SPECTROMETRY OF HERBAL EXTRACTS

G.E. Morlock[1], E.A. Crawford[2], A.N. Shikov[3], O.N. Pozharitskaya[3], E.S. Chernetsova[1]

[1] Justus-Liebig-University of Giessen, Giessen, Germany
[2] IonSense Inc., Saugus, MA, USA
[3] St-Petersburg Institute of Pharmacy, St-Petersburg, Russia
Gertrud.Morlock@ernaehrung.uni-giessen.de

The new ID-CUBE ion source, based on the Direct Analysis in Real Time (DART) technology and installed to a Q Exactive benchtop Orbitrap mass spectrometer, was investigated for the first time for its capabilities for herbal analysis. On the metal grid of the OpenSpot Cards, aliquots of herbal extract solutions were applied and dried. Then, the cards were manually introduced into the ion source. The sample preparation procedure took less than 3 minutes and was just limited by the drying duration. The application of larger volumes (> 5 µL) was possible for an increased detectability in trace analysis. For mass spectrometric analysis, the ionization of the analytes from the card was stimulated within 20 seconds by applying an electric current directly to the metal grid. This enhanced the analyte desorption into the gas flow of metastable helium atoms flowing from the ID-CUBE to the orifice of the mass spectrometer.
Within the investigation of propolis extracts and Bergenia crassifolia L. green leaf extracts, elemental compositions were assigned to abundant signals in the respective mass spectra. The major phenolic components were confirmed by their [M-H]- ions. The results obtained demonstrated the high potential and perspectives of this new ID-CUBE-HRMS technique for herbal analysis, especially for the confirmation of known components. Moreover, it was demonstrated that, owed to the exact mass values, molecular formulae suggested were helpful for further identification of unknown components.

DIRECT SCREENING AND QUANTITATIVE ANALYSIS OF CARBENDAZIM AND OTHER PESTICIDES IN FRUIT JUICES BY AMBIENT IONIZATION MASS SPECTROMETRY

Elizabeth Crawford, Brian Musselman

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Routine pesticide and fungicide use in the United States, as well as abroad warrants the need for analytical techniques that can rapidly screen and quantify residues in order to efficiently monitor produce products before reaching the consumer market. The allowable residue levels of chemical residues including pesticides and fungicides on produce are governed by the US EPA Code of Federal Regulations that sets tolerance levels based on the commodity. Of particular interest in the United States, carbendazim was found in imported orange juice and orange juice concentrates from Brazil, where the use of that fungicide is legal and therefore rapid product screening would increase

consumer safety in the US and worldwide. The Direct Analysis in Real Time (DART) ambient ionization technique offers the ability to rapidly screen the surface of produce for pesticides by a direct swabbing method and permits direct analysis of fruit juices in seconds. With automated sample introduction rapid screening and quantitative measurements can be completed using DART ionization coupled to high resolution accurate mass and triple quadrupole mass spectrometers.
Limits of detection using the DART ionization quantitative method coupled with Q Exactive and API 4000 QTRAP mass spectrometers were below 10 ppb for a 10 pesticide mixture detected in a variety of fruit juices, as well as for carbendazim directly analyzed from fruit juices. A number of the orange juices from the EU (5 juices), India (4 juices) and USA (3 juices) were screened for carbendazim and three juices all purchased in the EU tested positive for the fungicide at levels ranging from < 5 ppb up to 21 ppb.

NEW DART DETECTORS: ION MOBILITY SPECTROMETRY

Facundo M. Fernandez, Joel Keelor and Prabha Dwivedi

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facundo.fernandez@chemistry.gatech.edu

DART ionization has attracted significant attention due to its high-throughput and straightforward operation, simple to interpret spectral information and direct ionization capabilities. DART has been shown to be a powerful tool for screening for the presence of pesticides, chemical warfare agents, food authentication, and counterfeit drug detection, among other applications. Fieldable applications of DART would require its coupling to fieldable detectors. Because field portable mass spectrometers are still in the initial stages of development, atmospheric pressure drift tube IMS (DTIMS) has been used as an alternative, and successfully deployed in a wide variety of field scenarios. The primary appeal of DTIMS is its low cost, small size, weight and power consumption, and lack of a need for vacuum, advantages that come at the cost of somewhat reduced resolving power when compared to MS. DTIMS works by subjecting ions to a time-invariant electrical field and an opposing drag force exerted by a flow of purified bath gas, typically nitrogen. Ions are gated into a drift tube by means of a Bradbury-Nielsen type ion gate, creating a discrete ion packet that drifts as a swarm towards a Faraday plate detector. Ion gating can be implemented in more sophisticated ways, by means of direct or inverse multiplexing of the ion beam using arbitrary digital sequences.
In this presentation we discuss the different types of ion mobility detectors, in standalone mode or coupled to mass spectrometers, and the different types of interfaces that we are developing for successfully coupling DART to DTIMS. Direct in-situ ionization within the electric field gradient of the instrument enhances sensitivity and provides a safe sampling strategy. Alternatively, sampling in transmission mode can produce more stable signals with better reproducibility. Depending on the volatility of the analyte and the temperature of the system, time-dependent analysis can be performed to help discriminate between analytes. Other potential implementations for DART-DTIMS, such as the coupling of DART with IR laser ablation are also presented.

RAPID GENERATION OF FATTY ACID PROFILES USING DIRECT ANALYSIS IN REAL TIME (DART) MASS SPECTROMETRY

Brian Musselman, Jordan Krechmer, Joseph LaPointe, Elizabeth Crawford

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999 Broadway, Suite 404
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musselman@ionsense.com

Determination of the fatty acids in edible oils is often time consuming activity. Analytical methods for determination of methyl esters derived from saponification of triglycerides rely on GC and GC/MS for accurate quantitation of the individual acids in order to characterize the oil. We have investigated the potential of using ambient pressure desorption ionization to rapidly determine the fatty acids derived from the mixing concentrated ammonium hydroxide directly with various edible oils detecting the reaction products by using direct analysis in real time-mass spectrometry (DART-MS).
The rapid sampling of DART-MS permits monitoring of reaction products in seconds per sample using only a few microliters of sample. A rapid desorption system that allows for both detection of the acids by negative ion detection of the deprotonated molecule. The unreacted triglycerides can also be determined using a unique sampling system for efficient desorption of molecules from a stainless steel wire mesh that is then positioned between the DART source and the API-inlet of the mass spectrometer. The mesh is attached to a variable-current power supply that can deliver sufficient current to heat the sample at a rate > 20X faster than the conventional DART cartridge heater.
As monitoring of the production of fatty acids is completed in seconds per sample the method shows promise as a tool for detection of low and moderate levels of contaminants, monitoring the progress of biofuel production, detection of adulterants and non-specific threats. Optimum reaction conditions for generation of the products will be discussed. Analysis of reaction products with a Thermo Exactive high resolution accurate mass spectrometer permits ultrahigh resolution of reaction products while also permitting accurate mass determination of those ions. Analysis of a collection of edible oils for their fatty acid content will be presented.

JUNE 19, 2012 (11:00–12:00)

WATERS – VENDOR WORKSHOP: WATERS' UNIVERSAL ION SOURCE ARCHITECTURE – ASAP & APGC

ASAP – RAPID FINGERPRINTING IN FOOD AND BEVERAGE PRODUCTS

Sandra Rontree[1], Jean-Marc Joumier[2]

[1] Waters Corporation, Mass Spectrometry Headquarters, Manchester, UK
[2] Waters Corporation, European Headquarters, St Quentin, France

A low-cost alternative, the ASAP source has proven to be a useful tool for the rapid direct analysis of volatile and semi-volatile solid and liquid samples using atmospheric pressure ionization. The ASAP technique utilizes heated nitrogen desolvation gas to vaporize the sample and a corona discharge for ionization. It is capable of ionizing low polarity compounds not amenable to ESI, APCI, and APPI at high sensitivity. It can also be used to analyze complex samples without the need for sample preparation or even chromatographic separation.

The ASAP Probe and the range of MS systems, such as time-of-flight and quadrupole MS, combined with software platform, were used to successfully screen the ingredients that are used within the food and dietary supplements industry.

This approach is easy to adapt in any food production or QC environment to help rapidly analyze incoming samples. The end result is that the operating cost of labs can be substantially reduced.

APGC - ADVANTAGES OF ATMOSPHERIC PRESSURE GAS CHROMATOGRAPHY IONIZATION IN EXTRACTABLE IDENTIFICATION

Sandra Rontree[1], Jean-Marc Joumier[2]

[1] Waters Corporation, Mass Spectrometry Headquarters, Manchester, UK
[2] Waters Corporation, European Headquarters, St Quentin, France

Atmospheric pressure gas chromatography (APGC) is a new interface that allows a GC to be coupled to a time of flight (TOF) or quadrupole time of flight (QTOF) mass spectrometer. This interface has 2 advantages over a conventional electron ionization (EI) or chemical ionization (CI) GCMS: it ionizes the sample with an atmospheric pressure chemical ionization (APCI)-like mechanism that can give good ionization for samples that are not ionized well under EI or CI conditions. In addition, it allows collection of accurate mass data, and in the case of the QTOF, accurate mass of fragments which in turn makes it possible to identify the structure of compounds not in the library. This technique is especially useful for suspected degradants of known compounds.

Extractable data are presented for several packaging materials extracted in IPA. The extracts were analyzed by EI and CI on a conventional GCMS and with an APGC interface on a Waters Xevo QTOF mass spectrometer.

The results of each technique were compared to demonstrate that the APGC source provided structural information for peaks which were not sufficiently defined by conventional GCMS (EI or CI).

JUNE 19, 2012 (12:00–13:00)

Thermo SCIENTIFIC

Part of Thermo Fisher Scientific

THERMO SCIENTIFIC – VENDOR WORKSHOP: NEW SOLUTIONS FOR HIGH THROUGHPUT FOOD SCREENING USING DART-ORBITRAP TECHNOLOGY

EXACTIVE PLUS AND Q EXACTIVE ORBITRAP PLATFORMS FOR DIRECT SCREENING AND QUANTITATIVE ANALYSIS OF CHEMICAL RESIDUES WITH DART IONIZATION

Elizabeth Crawford, Brian Musselman

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Routine pesticide and fungicide use in the United States, as well as abroad warrants the need for analytical techniques that can rapidly screen and quantify residues in order to efficiently screen products against maximum residue limits (MRLs) before reaching the consumer market. Of particular interest in the United States, carbendazim was found in imported orange juice from Brazil, where use of that fungicide is legal and rapid screening of produce commodities worldwide would increase consumer safety. Illegal dyes in food are also of concern, as well as regulated phthalates in a wide range of consumer products fueling the need for regulatory bodies and manufacturers to efficiently screen for many contaminants simultaneously.

The Direct Analysis in Real Time (DART) ambient ionization technique offers the ability to rapidly screen the surface of objects either by direct interrogation or by a swabbing method and permits direct analysis of liquid samples in seconds. With automated sample introduction screening and quantitative measurements are realized using DART technology coupled to high resolution accurate mass Orbitrap based mass spectrometers.

ADVANCES IN BENCH-TOP ORBITRAP MASS SPECTROMETRY: A REAL ALTERNATIVE TO TIME OF FLIGHT-MS

Michal Godula, Markus Kellmann

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Screening of contaminants and residues in food is of great importance in regulated environments such as food control labs, contract labs and routine quality control. Due to the broad variability of physico-chemical properties of pesticides the trend is to employ simple sample preparation procedure to maintain the recovery of the broad range of analytes and to streamline or even eliminate the sample preparation procedures to lower analysis costs and increase lab throughput. This unavoidably leads to the fact that final extracts injected into the chromatographic systems contain significant amounts of coextracts. For the chromatographic determination it is therefore essential to apply the systems with high selectivity and low achieved detection limits.

Traditionally the analysis of low levels of pesticides has been carried out using selected reaction monitoring (SRM) scanning using triple quadrupole mass spectrometer instruments. This approach has significant advantages with respect to achieved performance but also certain limitations such as limited number of compounds per analysis, little possibility to scan for unknown compounds at high levels and necessary system optimization to run specific set of compounds.

Because of these limitations, in residue analysis there is currently a trend towards applying the full scan MS acquisition experiments using instruments delivering high mass accuracy and resolution.

As already documented, high resolving power of the mass spectrometers based on Orbitrap™ and their ultimate mass accuracy provide unique advantages in the screening and quantitation of low levels of contaminants in complex food matrices [1].

The presentation will demonstrate how the recent developments in the instrumental techniques and specifically Orbitrap technology allow to improve the methods used in food labs to detect low levels of contaminants. The presentation will summarize recent improvements in the Orbitrap technology with respect to the application of DART ionization for direct analysis of high matrix samples.

[1] Kellman et al, J Am Soc Mass Spectrom 2009, 20, 1464–1476

JUNE 19, 2012 (12:00–13:00)

Agilent Technologies

AGILENT TECHNOLOGIES – VENDOR WORKSHOP: AMBIENT MS USING THE IONSENSE DART AND ID-CUBE WITH AGILENT'S PORTFOLIO OF MASS SPECTROMETERS

AMBIENT MS USING THE IONSENSE DART AND ID-CUBE WITH AGILENT'S PORTFOLIO OF MASS SPECTROMETERS

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The seminar will describe the use of DART and ID-Cube with the many mass spectrometers that Agilent offers. This will include discussion of ambient MS with single quadrupole, triple quadrupole, time-of-flight, and hybrid quadrupole time-of-flight mass spectrometers. Examples of pesticides in food, pesticides in natural products, and characterization of natural products will be given.

JUNE 20, 2012 (11:00–12:00)

Advion

ADVION – VENDOR WORKSHOP: LIQUID EXTRACTION SURFACE ANALYSIS (LESA), INNOVATIVE UPGRADE TECHNOLOGY FOR THE TRIVERSA NANOMATE®

LIQUID EXTRACTION SURFACE ANALYSIS (LESA), INNOVATIVE UPGRADE TECHNOLOGY FOR THE TRIVERSA NANOMATE®

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LESA (Liquid Extraction Surface Analysis) is a surface-directed MS based analyses technique, where a liquid micro junction sampling probe is used to extract the analytes directly from a surface. The enabling technology is the TriVersa NanoMate®, a well-established robotic platform for the automated delivery of samples to mass spectrometers via a chip-based nano-electrospray emitter. It enables beside LESA the online-coupling to HPLC systems as well as parallel fraction collection and direct infusion from sample plates at low flow rates by retaining high spray stability. It allows analysts to obtain more information from complex samples than with LC/MS alone. LESA is used by many laboratories for a wide range of application areas and surfaces, like pesticides analyses on food surfaces, plant metabolite studies, drug metabolite distribution studies on tissue sections, peptides and small molecules sampling from solid-phase extraction (SPE) cards and also for analyses from dried blood spots (DBS) on paper, TLC plates and Maldi targets for complementary information by ESI. In summary, the scientific community adopted this new surface analysis method in a very fast manner and the diversity of published studies gives evidence for the practical usefulness of this approach.
This hands-on workshop shows how the LESA technique works in detail:
• Introduction of the TriVersa NanoMate technology
• Demonstration of the ChipSoft Software including the LESA setup
• Liquid Extraction Surface Analysis in action

JUNE 20, 2012 (11:00–12:00)

LECO – VENDOR WORKSHOP: GC×GC–TOF MS AND ULTRA HIGH RESOLUTION TOF MS WITH FOLDED FLIGHT PATH (FFP™) TECHNOLOGY IN FOOD-RELATED APPLICATIONS

ULTRA HIGH RESOLUTION TOF MS WITH FOLDED FLIGHT PATH (FFP TM) TECHNOLOGY IN FOOD-RELATED APPLICATIONS

Tomáš Kovalczuk

LECO European Technical Centre Prague, Czech Republic

The excellent operational parameters of ultra performance mass spectrometry – selectable mass resolution up to 100,000 (FWHM) and accurate mass data (<1 ppm) - are enabled by utilizing a unique multi-reflecting time-of-flight mass spectrometry technology referred to as a Folded Flight Path (FFPTM). Key to this FFP technology are the two opposing, high precision rectangular gridless ion mirrors and an array of gridless periodic focusing elements separating them. The FFP system permits a long flight path in a compact design (up to 64 reflections corresponding to a flight path of 40 m). The novel FFP technology enables hyphenation not only with the high-speed chromatographic techniques (GC UHPLC) to provide separations, but also with ambient MS, such as DART or DESI. The capabilities of this novel technology will be demonstrated on food-related applications.

UTILIZATION OF COMPREHENSIVE GAS CHROMATOGRAPHY COUPLED TO TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE DETERMINATION OF FOOD ORIGIN

Ivan Špánik

Slovak Technical University, Slovakia

Determination of honey origin is very important for the purpose of authenticity control. In this work a GC×GC-TOF MS technique has been applied to identify honey volatiles and select the important markers of geographic origin of the honey.

ORAL SESSIONS

(L-1 – L-19)

L-1
DART-INSTRUMENTATION, APPLICATIONS AND FUNDAMENTALS

Facundo Fernandez[1*], Glenn Harris[2], Carrie Pierce[3], Joel Keelor[4], Rachel Bennett[5], Prabha Dwivedi[6]

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Ambient or “open air” surface sampling techniques are a group of ion generation approaches that can be readily coupled to mass spectrometric detectors for MS analysis of target compounds. These technologies have been coupled to a variety of mass spectrometers equipped with atmospheric pressure interfaces with only minor modifications, enabling unknown identification via fragmentation pattern matching to databases, elemental formula determination via accurate mass measurements, multi-analyte quantitation, spatially-resolved measurements, and selective ionization enhancement for target compounds of interest. Ambient MS sampling/ionization techniques such as Direct Analysis in Real Time (DART) and Desorption Electrospray Ionization (DESI) have grown in popularity because they enable the sampling of analyte under atmospheric pressure conditions from both liquid and solid phases remotely from the mass analyzer, have been used to investigate objects or surface features of a wide range of shapes, sizes and textures, can perform qualitative or quantitative analysis with no or minimal sample preparation such as dissolution, grinding, extraction or pre-concentration, and can conduct all these operations in real time with high sensitivity and minimal unwanted ion fragmentation. DART uses a point-to-plane atmospheric pressure glow discharge to generate metastable species in a chamber that is physically separated from the ionization region. The discharge support gas, containing metastables, is heated and directed through a grid electrode that filters ions and electrons to mitigate ion-ion and ion-electron recombination of species generated within the DART ionization source. DART can be used to sample gases, liquids and solids. In laboratory settings, gases are directly injected into the ionization region following the grid electrode, whereas liquids are generally sampled by dipping a glass capillary in them and placing it in the ionization region. Solids can be directly analyzed by holding them with tweezers and exposing them to the ionizing gas, or in transmission mode geometry (useful for transmissive samples, such as meshes). Powders can be mixed with metal particles, adhered to a permanent magnet and exposed to the DART gas. Foam swabs, solid-phase extraction materials, and PDMS coated stir bars, can also be directly placed within the DART ionization region. In this presentation we will discuss advances from our group in (a) using commercial DART sources to screen falsified artemisinin combination therapy drugs found in Africa, (b) development of an electrothermal vaporization interface for DART, (c) developing an imaging laser-ablation/DART MS system for imaging 2D-HPTLC plates, and (d) using DART for diagnostics and metabolomic studies.

Keywords: Ambient mass spectrometry, DART

L-2
ATMOSPHERIC PRESSURE SOLIDS ANALYSIS PROBE (ASAP) – INSTRUMENTATION AND FUNDAMENTALS

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This presentation will introduce the Atmospheric pressure Solids Analysis Probe (ASAP) as a rapid means of sample introduction to a mass spectrometric detector. An instrumental overview will be given, sample introduction described and the principles of ionisation discussed. The advantages of the technique will then be highlighted using examples from the application areas of food contact materials, pesticides and food additives and contaminants.

Keywords: ASAP, fundamentals

L-3
INTRODUCTION TO DESI MASS SPECTROMETRY

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Desorption electrospray ionization (DESI) was invented by Graham Cooks and co-workers and the first ambient mass spectrometry (MS) technique established. The set-up is relatively simple and can be constructed from an old nano ESI source, or purchased at Prosolia: a pneumatically assisted electrospray is producing charged sovent droplets which are directed at an angle to the sample surface under investigation at ambient conditions. Secundary ions are formed from the wetted surface according to a droplet pick-up mechanism followed by electrospray like ion formation and sampled by the inlet of the MS. In this introductory presentation DESI principles will be explained, operating parameters discussed and different applications shown from the authors laboratory.

Keywords: DESI, mass spectrometry, introduction

Acknowledgement: The national science foundation NWO is acknowledged for granting a DESI MS system to Wageningen University.

L-4
LIQUID EXTRACTION SURFACE ANALYSIS (LESA): BASIC PRINCIPLE AND REVIEW OF RECENTLY PUBLISHED STUDIES

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LESA-functionality was recently made available as an upgrade for the TriVersa NanoMate®, an earlier established robotic platform for the automated delivery of samples to mass spectrometers via a chip-based nano-electrospray emitter. The equipment enables the user to generate a calibrated picture scan of the surface of interest and to select directly on the picture which positions should become successively addressed in a fully automated mode. On every position, an integrated pipette robot applies small quantities of solvent and takes it up a few seconds later for the chip-based infusion of the extract into the mass spectrometer. Since the general proof of the concept (1), LESA has been used by many laboratories for a wide range of application areas: Lipid profiles were generated directly from atherosclerotic plaques (2), pesticides were detected on food surfaces (3), haemoglobin variants were analyzed from series of dried blood spots (DBS) (4), plant metabolite containing exudates were investigated from maize roots (5), peptides and small molecules were sampled from solid-phase extraction (SPE) cards (6), drug metabolite distribution studies were done on rat tissue sections (7), and polymer additives as well as degradation products such as melamine were discovered in metal coatings (8). In summary, the scientific community adopted this new surface analysis method in a very fast manner and the diversity of published studies gives evidence for the practical usefulness of this approach.

(1) Kertesz V & Van Berkel GJ (2010): J. Mass Spectrom. 45(3), 252-60.
(2) Stegemann C et al. (2011): Genet. 4, 232-242.
(3) Eickel D & Henion J (2011): Rapid Commun. Mass Spectrom. 25, 2345–2354.
(4) Edwards RL et al. (2011): Anal. Chem. 83, 2265–2270
(5) Robert CAM et al. (2012): Ecology Letters 15, 55–64.
(6) Walworth MJ et al. (2011): Rapid Commun. Mass Spectrom. 25, 2389–2396.
(7) Schadt S et al. (2012): Drug Metab Dispos 40, 419-425.
(8) Paine MRL et al. (2012): Rapid Commun. Mass Spectrom. 26, 412–418.

Keywords: LESA, NanoMate, Surface Analysis, ESI-Chip, Nanospray

L-5
DART-TOF-MS: A TIME-SAVER IN ANALYTICAL CHEMISTRY

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Some of the so called “ambient ionization mass spectrometry” techniques are still restricted to lab-made instrumentation, some of them like Direct Analysis in Real Time (DART) first presented by Cody et al. [1] or desorption electrospray ionization (DESI) developed by Cooks [2] have been commercialized throughout the last years. Major fields of application of these two techniques are the direct analysis of solids with numerous reports, many of them related to food analysis, pharmaceutical analysis, but also imaging of surfaces (such as tissue cuts or TLC plates) is possible. In the present paper we would like to present two specific applications of DART slightly beyond its accepted usage.Techniques like solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are widely used for sample preparation in particular for the extraction of substances (e.g. contaminants) from a wide range of matrices. Subsequently the stir bars os SPME fibres are analyzed by GC-MS after thermodesorption or elution with an appropriate solvent. A common drawback of this approach is that its time consuming particularly when analyzing not-contaminated or irrelevant samples. DART-TOF-MS is a perfect tool for the rapid (semi-quantitative) screening of stir bars [3] or SPME fibres. Thereby for example environmental water samples can be categorized in contaminated ones, requiring further quantitative analysis by GC or LC and non contaminated ones without need of further testing. A second non-routine application of DART-TOF-MS is its usage as a detector for liquid phase separation such as HPLC or liquid phase sample introduction (such as flow injection analysis (FIA)) techniques. DART has a much less pronounced tendency towards ion suppression (when compared with electrospray ionization (ESI)); a fact that can be exploited in different ways; first the use of non-ESI compatible eluents in LC [4] and second, the analysis of samples with complex matrices often accompanied by unwanted ion suppression effects [5]. HPLC or FIA DART-TOF-MS might be a useful tool for the very fast screening of samples affected with problematic matrix properties. Substantially reduced ion suppression (compared to ESI and APCI) would allow the direct analysis of sewage environmental samples, food samples and even biological fluids without pre-treatment and with no or only minimal chromatographic separation [6].

[1] R. B. Cody, et al. Anal. Chem., 2005, 77, 2297.
[2] Z. Takats, et al. Science, 2004, 306, 471.
[3] M. Haunschmidt, et al. Anal. Bioanal. Chem., 2010, 3790, 269.
[4] W. Eberherr, et al. Anal. Chem., 2010, 82, 5792.
[5] S. Beißmann, et al. J. Chromatogr. A, 2011, 1218, 5180.
[6] I. Hintertseiner, et al. submitted.

Keywords: DART, TOF-MS, flow injection analysis, ionization suppresssion, HPLC

L-6

THE USE OF HIGH RESOLUTION MASS SPECTROMETRY (SYNAPT G2 HDMS) WITH ASAP SAMPLE INTRODUCTION FOR THE ANALYSIS OF PLASTICISERS IN THE GASKETS OF FOOD JAR LIDS

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Plasticisers are added to the gaskets of glass jar lids to increase the flexibility of the PVC polymer used and they can be present in high proportions. There are many different plasticisers available and EU Regulations contain a list of additives permitted in gaskets intended for food contact applications and assign specific migration limits for several plasticisers. This presentation will describe a screening method using ASAP sample introduction followed by high resolution mass spectrometric detection using the SYNAPT G2 HDMS system for a range of plasticisers in gaskets from lids for glass jars used for foodstuffs.

Keywords: ASAP, plasticisers, SYNAPT G2 HDMS

L-7
HPTLC-DART-MS FOR FOOD SAFETY AND NATURAL PRODUCTS CONTROL

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Direct Analysis in Real Time mass spectrometry (DART-MS) is a rapidly emerging field since its start in 2005 [1]. Its main advantage over other mass spectrometric techniques is the minimization or even absence of the sample preparation. For hyphenation with planar chromatography [2], and therein, especially high-performance thin-layer chromatography (HPTLC), it is promising because the shape of a spot is not distorted by a solvent of high elution strength. In 2009, a new version of the DART ion source, called DART-SVPA, was introduced, which allowed adjusting the angle of the DART gas stream and the use of a motorized x-rail. This angled source significantly extended the general capabilities of DART-MS, and in 2011, the access was extended in three different dimensions by a wide, x,y,z-adjustable carrier table [3]. The most favorable conditions for the HPTLC-DART-MS set-up are still under investigation. The visualization of the DART gas impact region onto a substrate was developed based on a chemical reaction upon heating. Owed to the hot DART gas, the gas impact generated a colored product. Such an option for visualization is important for optimal alignment required for quantitative HPTLC-DART-MS, as the horizontal scanning along the socalled hRF substance window allows a rapid evaluation of all samples on the plate. Compared to DIP-it DART-MS, the hyphenation with planar chromatography would allow a matrix-free analysis of extracts. As both methods (DART and HPTLC) are fast analytical methods, their combination would be ideal for food safety and natural products control. First results on HPTLC-DART-MS analysis of food contaminants, propolis and plant extracts will be reported. Current limitations and further developments required will be discussed.

[1] R.B. Cody, J.A. Laramée, H.D. Durst, Anal. Chem. 77 (2005) 2297–2302.
[2] G.E. Morlock, E.S. Chernetsova, Centr. Eur. J. Chem. 10 (2012) 703-710.
[3] E.S. Chernetsova, A.I. Revelsky, G.E. Morlock, Rapid Commun. Mass Spectrom. 25 (2011) 2275-2282.

Keywords: HPTLC-DART-MS, planar chromatography

L-8
DART-MS AS A TOOL FOR MYCOTOXINS SCREENING

Milena Zachariasova[1], Lukas Vaclavik[2], Vojtech Hrbek[3], Zbynek Dzuman [4], Jana Hajslova[5*]

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Direct analysis in real time (DART) ionization coupled with an ultra-high resolution mass spectrometer based on orbitrap technology (orbitrapMS) was employed for high-throughput quantitative analysis of multiple mycotoxins in cereals. After initial evaluation of ionization efficiencies for major groups of mycotoxins achievable by DART technology, sample preparation procedure and instrument parameter settings were optimized to obtain sensitive and accurate determination of most intensively ionizing toxins. The lowest calibration levels (LCLs) estimated for the particular analytes ranged from 50 to 150 μg/kg. For quantitative analysis, using of matrix-matched standards and employing of 13C-labeled internal standards were compared and discussed. Very good recoveries (100–108%) and repeatabilities (RSD 5.4–6.9%) at spiking level of 500 μg/kg were obtained by using the internal standard correction. As far as matrix-matched calibration was used, recoveries and repeatabilities were in the ranges of 84–118% and 7.9–12.0% (RSD), respectively. The trueness of data obtained for deoxynivalenol and zearalenon in wheat/maize by DART–orbitrapMS was demonstrated by analysis of certified reference materials (CRMs). Good agreement of results obtained by this novel approach with data generated by validated ultra-high pressure liquid chromatography–time-of-flight mass spectrometry method was documented.
In addition to quantitative (target) analysis, the DART–orbitrapMS technology was used also for the metabolomic profiling of cereals. Various sets of barley (fungicide treated vs. untreated, different barley varieties) could be distinguished by this technology by employing of advanced chemometric and statistical data processing methods independently on the mycotoxins content.

Keywords: DART-MS, mycotoxins, cereals

Acknowledgement: The study was undertaken under the financial support of following project QI111B044.

L-9
INTRODUCTION TO FOOD FORENSICS

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The food chain is a global complex and vulnerable for contamination by natural sources and human behaviour. Natural biotoxins, pesticides and veterinary drugs residues, and environmental pollutants are examples of frequently occurring chemical contaminants in the food chain. For legal and regulated substances routine control systems have been established by producers, producer organisations, and (inter)national authorities. However, the food chain is also highly vulnerable for fraud, for example fraud with bulk ingredients such as carbohydrates, fats and proteins; specific fraud with product authenticity; and fraud with illegal substances and/or illegal production methods. An example of the first category is the melamine scandal, and an example of the latter is the use of growth promoters in meat production such as anabolic steroids or clenbuterol. In these case different economic, trade and health laws and regulations can be violated. It is hard to know where, when and how fraud will occur. One should look for both known and unknown chemical substances. Some compounds might be deliberately synthesized in order to circumvent Detection and you won't find those in literature or patent databases. Therefor targeted analysis methods are only suitable to a limited extent. A rapid first chemical profile by NMR, mass spectrometry (MS), or biological tests might provide a first guess about identity, toxicity and relevance. In this presentation a multi-disciplinary approach will be advocated for the analysis of seized preparations, additives, and hair and dust samples. Also recent ambient MS tools such as DART and DESI can have a role.

Keywords: Food, fraud, forensics

Acknowledgement: This work is financially supported by the Dutch Ministry of Economic Affairs, Agriculture & Innovation.

L-10
INVESTIGATION OF HORMONES IN TISSUE USING IMAGING DESI-MS

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In this presentation the feasibility of desorption electrospray ionization (DESI) mass spectrometry (MS) for the imaging of intact esters of anabolic steroids in bovine tissue is presented using a linear ion trap in both full scan and MSn mode. The resolution of the DESI probe was investigated by scanning permanent marker lines drawn at various distances, using an x-y-z positioner. In a next experiment, slices of beef injected with a hormone cocktail were scanned using DESI-MS. All hormones could be directly detected in the sample and the injection spot could be well defined. The potential of this DESI approach is clearly demonstrated by imaging of MS data from bovine tissue injected with levels of steroid esters which can occur in samples from illegally treated animals. The technique offers great potential for quick screening of tissue samples from hormone injection sites. It is time-saving, as no elaborate clean-up procedures are needed, and can be applied when no other sample material (e.g. urine, hair) is available. Moreover, as opposed to extraction of the whole sample, with the DESI approach material remains for contra-investigation.

Keywords: Desorption, electrospray, injection sites, bovine tissue, hormone esters, resolution

Acknowledgement: Prof. dr. Ron Heeren and dr. Ivo Klinkert from AMOLF Amsterdam for help with the imaging software, The DESI-MS facility was granted by the Dutch Science Foundation (NWO) to Wageningen University, This project was financially supported by the Dutch Ministry of Economic Affairs, Agriculture and Innovation

L-11
APPLICATION OF DART–TOFMS IN CHICKEN FEEDING HISTORY

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In recent years, interest in meat authenticity has increased. Many consumers are concerned about the meat they eat and accurate labelling is important to inform consumer choice. Authentication methods can be categorized into the areas where fraud is most likely to occur: (i) meat origin (sex, meat cuts, breed, feed intake, slaughter age, wild vs. farmed meat, organic vs. conventional meat, geographical origin), (ii) meat substitution (meat species, fat, protein), (iii) meat processing treatment (irradiation, fresh vs. thawed meat, meat preparation), and (iv) non-meat ingredient addition (additives and water) [1]. In more detail, there are various means of tracing animal feed intake. Traceability is possible because different chemical constituents are present in feeds such as milk, pasture, hay, maize, and concentrate (mixed dried constituents), which upon consumption shows up as different chemical constituents or metabolites forms in the animal's blood and fat [1]. Up now published studies dealing with feed intake were focused on the determination of carotenoids, xanthophylls, carotenes, composition of fatty acids in meat, volatile compounds, vitamins and terpenes. Recently, metabolomics centred around the detection of the broadest possible range of small molecules (<1,500 Da) in complex biological matrices using a single or small number of analyses has also emerged as a field of interest in food analysis [2]. Beside of conventional techniques (GC–MS, LC–MS, NMR) used for metabolomic fingerprinting/profiling, ambient desorption ionisation techniques represent a novel solution for direct sample examination in the open atmosphere, with minimal or no sample preparation requirements and remarkably high sample throughput [3]. In this study, the challenge to develop a rapid method for metabolomic fingerprinting/profiling of chicken muscle and feed for the authenticity/traceability purposes using a direct analysis in real time (DART) ion source coupled to a high-resolution time-of-flight mass spectrometer (TOFMS) has been addressed.

References
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[2] Wishart, D. S. (2008). Metabolomics: applications to food science and nutrition research. Trends in Food Science & Technology, 17, 482–493.
[3] Hajslova, J., Cajka, T., Vaclavik, L. (2011). Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis. Trends in Analytical Chemistry, 30, 204–218

Keywords: DART–TOFMS, chicken, feed, metabolomics

Acknowledgement: The financial support of the Ministry of Education, Youth and Sports of the Czech Republic (projects MSM 6046137305, MSMT No. 21/2012) and the Ministry of Agriculture of the Czech Republic (NAZV-QI91B306) is acknowledged.

L-12
AUTHENTICATION OF FOOD AND FEED LIPIDS

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Fats and oils represent an important group of food/feed commodities which are, with regard to their production scale, of relatively high commercial value. Extra virgin olive oil, sesame oil, milk fat and lard are examples of the most highly prized commodities of this category. However, under certain conditions, fats/oils might be a source of toxic compounds such as persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), 3-chloropropane 1,2-diol (3-CPD) esters etc. The contamination might be due to their environmental contamination or improper processing practices. Another indicators of poor quality are products of hydrolytic and /or (auto)oxidation reactions taking part during their heat-treatment and long term storage. In many cases, lipids containing hazardous components are cheap admixtures used for adulteration motivated by maximizing profit. In this context, the identification of the origin of such food/feed ingredients and respective food sources is of a high importance measure enabling protection of consumers´ health.
In the current presentation, the use of an ambient mass spectrometry (AMS)-based approach for complex quality and authenticity assessment of various oils and fats. of both plant and animal origin, will be discussed. The application potential of the challenging technique, employing Direct Analysis in Real Time ion source (DART) coupled with high resolution mass spectrometer (HRMS) will be demonstrated on the following case studies:

- Metabolomic fingerprinting of oils, fats, meat, milk and milk-based foods for authenticity assessment, with the use of advanced chemometric tools for data processing.
- Qualitative and quantitative high-throughput assessment of oxidation extent in vegetable oils
- used for frying
- Monitoring of fish oil-based supplements quality/ stability

Acknowledgements
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L-13
UTILIZATION OF AMBIENT MASS SPECTROSCOPY TECHNIQUES TO AID IN BOTANICAL AUTHENTICATION

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The area of botanical authentication techniques has evolved from utilizing many classical pharmagocognostic techniques such as macro/microscopic identification to using genetic profiling and chromatographic fingerprinting methods (TLC, HPTLC, GC, and HPLC). However these techniques often require significant sample preparation and, for chromatographic fingerprinting, the development of an appropriate analytical method. The use of broad-spectrum spectroscopic fingerprinting techniques such as MS, IR, NMR has been growing significantly over the last few years and is emerging as a viable alternative to classical chromatographic fingerprinting techniques. The utilization of Ambient Mass Spectroscopy (AMS) to provide a rapid evaluation tool for the authentication of botanicals would prove to be beneficial for the scientific assessment of these materials as well as for potential commercial applications. Using AMS we were able to quickly develop a fingerprint profile for several botanicals and use the generated data to differentiate between various species. For example it was possible to differentiate the two main species of chamomile used in commerce, German chamomile (Matricaria recutita L.) and Roman chamomile (Chamaemelum nobile (L.) All.). The presentation will include several examples of how AMS has been applied to provide a fingerprint profile of botanicals and how this technique can aid in the authentication process.

Keywords: TOF MS, characterization, botanicals, pharmacognosy

L-14
UHPLC–MS AND DART-MS TECHNIQUES AS TOOLS FOR METABOLOMICS-BASED SCREENING OF ABIOTIC PLANT STRESS

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Low temperature tolerance is an important factor which determines geographical distribution of plant species and significantly affects the yield of major crops in respective climatic zones. The availability of rapid and reliable tools for monitoring of plants cold tolerance / susceptibility represents a critical condition for research aimed at breeding of cold tolerant crop plants. Therefore, we tested the application of metabolomics-based workflow employing ultra-high performance liquid chromatography–mass spectrometry (UHPLC–MS) and direct analysis in real time–mass spectrometry (DART–MS) instrumentation for high-throughput monitoring of response to low temperatures and screening of cold tolerance in Arabidopsis thaliana accessions. Metabolomic fingerprinting was performed (i) before and after two weeks of cold acclimation at 4°C and (ii) after freeze-thaw treatments at –4°C for 8 hours; methanolic extracts of leaves collected from parallel growing plants were examined. The generated data (chromatograms and mass spectra) were processed with the use of multivariate statistical analysis employing principal component analysis (PCA) and linear discriminant analysis (LDA). The PCA of metabolomic fingerprints revealed clear tolerance-dependent differences of both acclimated and freeze-thaw cycle treated plants. In the final stage of the study, measurements employing UHPLC coupled to quadrupole-time-of-flight mass spectrometry (QTOFMS) were performed in order to obtain data for identification of pre-selected marker compounds, characteristic for accessions with low, intermediate and high cold tolerance.

Keywords: Cold tolerance, metabolomics, chemometric analysis, LC-MS, DART-MS

Acknowledgement: The financial support from the Ministry of Education, Youth and Sports (projects OC10060 and MSM6046137305) is gratefully acknowledged.

L-15

THE POTENTIAL OF LC-HRMS METABOLOMICS FINGERPRINTING IN FOOD ANALYSIS: APPLICATION TO THE CONTROL OF FORBIDDEN SUBSTANCES

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Growth promoting practices for cattle fattening purposes are still encountered all around the world, for instance the use of clenbuterol in pigs, recombinant growth hormone in dairy cows and fish, natural steroids in cocktails' in bovines, or hypothetic but realistic anabolic strategies consisting either on upstream disruption of the hypothalamo-pituitary axis (secretagogues, …) or even worst on direct genes modification (gene doping). Detection of illegal practices classically relies on residue monitoring in a targeted approach and methods based on gas- or liquid chromatography coupled to (tandem) mass spectrometry are today considered as the state-of the-art. These strategies are however challenged when facing new xenobiotic growth promoting agents or new ways of application, such as the administration of low dose cocktails. In this context, screening strategies allowing detection of the physiological response resulting from anabolic compounds administration are promising approaches to detect their misuse. Metabolomics is one of the approaches allowing profiling biological matrices to reveal biological effects of a drug. This emerging tactic has allowed highlighting candidate biomarkers which have been implemented in a robust statistical model to screen for anabolic treated bovines with different classes of compounds (various steroids, beta-agonists...).

Keywords: Metabolomics, chemical food safety, growth promoters, LC-HRMS

L-16
PROBING PLANTS BY DESI AND DART-MS: PROS AND CONS

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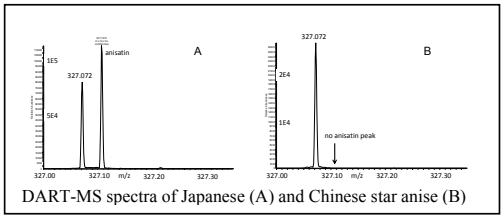
Over the last few years ambient mass spectrometry (MS) has developed into a mature niche within the MS field. The essence of ambient MS is that the sampling takes place in the open air, i.e. on your benchtop at atmospheric pressure and often without any sample preparation. Several applications of Direct Analysis in Real Time (DART), Desorption Electrospray Ionisation (DESI) MS and direct "plant spray" in the field of natural products chemistry are presented. Examples include amongst others wool dyed with flavonoids, alkaloids in Traditional Chinese Medicines (TCMs), the neurotoxic sesquiterpene lactone anisatin in star anise (see figure and [1]), diterpenes and alkylphenols in Ginkgo biloba and an essential oil. In particular DART-MS is a versatile, easy to handle and fast technique allowing even quantitative measurements of secondary plant metabolites. In combination with high-resolution MS it can be used for quality control, adulteration detection, metabolomics and screening of herbal products. It can also be hyphenated to HPLC or TLC. A comparison of DART and DESI-MS in terms of scope, figures of merit and limitations is made.



DART-MS spectra of Japanese (A) and Chinese star anise (B)

[1] Y. Shen, T.A. van Beek, F.W. Claassen, H. Zuilhof, B. Chen, M.W.F. Nielen, Rapid control of Chinese star anise fruits and teas for neurotoxic anisatin by Direct Analysis in Real Time (DART) high resolution mass spectrometry, J. Chromatogr. A, (2012) in press, http://dx.doi.org/10.1016/j.chroma.2012.03.058

Keywords: DART-MS, DESI-MS, plant-spray, Ginkgo, star anise

L-17
PROBING CHEMICAL DIVERSITY OF BACTERIA BY LESA

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There is always a medical need to explore new antibiotic agents to fight against resistant pathogenic bacteria. To support effective search for novel antibiotics from bacteria cultivated under diverse conditions we need a fast and cost-effective screening method. A combination of Liquid Extraction Surface Analysis (LESA), automated chip-based nanoelectrospray ionization, and high-resolution mass or tandem mass spectrometry using Orbitrap XL was tested as the screening platform. Actinobacteria, known to produce well recognized thiazolyl peptide antibiotics, were cultivated on a solid medium plate and the antibiotics were extracted by organic solvent mixtures and MS-analyzed directly from surfaces of colonies grown on the plate. Known antibiotics were correctly detected with high mass accuracy (<4 ppm) and further structurally characterized by tandem mass spectra, which were analyzed using fragmentation trees protocol recently developed in our laboratories. The method described in this paper is suitable for the direct screening of antibiotics produced by bacterial colonies on the cultivation plate and within 2 minutes compounds are extracted and detected at high mass accuracy at a cost of around 2 Euro per sample.

Keywords: Surface analysis, antibiotics, bacteria, high throughput

Acknowledgement: MPG Munich, Germany for financial support, Merck and Fundation MEDINA for bacteria collection, and Advion for technical support.

L-18

CHEMOMETRICS AND DIRECT INJECTION ANALYSIS OF VOLATILE COMPOUNDS BY PTR-TOF-MS: A TOOL FOR METABOLOMIC INVESTIGATIONS

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Sample classification and "explanatory" variable selection is a cutting edge problem in metabolomics. Among direct injection methods for the detection of volatile compounds, Proton transfer reaction-mass spectrometry (PTR-MS) is becoming more and more spread, especially after the coupling with time of flight detectors (PTR-TOF-MS). PTR-MS was proposed almost two decades ago for the rapid and high sensitivity monitoring of volatile compounds. It was immediately evident that food science and technology was one of its most interesting field of application given the role that volatile compounds play in food production, storage and consumption. We show that modern chemometric and data mining techniques, such as Random Forest, Partial Discriminant Analysis, Support Vector Machine, are well suited for addressing multiclass problems starting from fruit flavour profiles (by GC-MS) or fingerprints (by PTR-TOF-MS). Marker identification is successfully performed by recursive strategies such as Random Forest Recursive Feature Elimination. Moreover, regression methods, for instance LASSO and PLS, proved to be useful to link headspace, nose-space and sensory data from different analysis techniques. We present results from metabolomic studies by GC-MS and PTR-TOF-MS on i) raspberries: several cultivars having diverse levels of Botrytis susceptibility have been classified by the mentioned chemometric strategies and markers of Botrytis resistance have been identified; ii) apple cultivars and clones: markers for the discrimination of the apple clones based on their flavour profile have been identified; iii) grana cheeses and olive oils: we investigate the link between GC-MS profiles and PTR-TOF-MS fingerprint. Through these examples we will discuss the characteristics of the proposed strategy and show that it can provide a powerful tool for metabolomic.

Keywords: PTR-ToF-MS, volatile compounds, chemometrics, data mining, metabolomics

L-19
GENERAL STRATEGIES IN DATA HANDLING AND INTERPRETATION IN MASS SPECTROMETRY-BASED METABOLOMICS

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The metabolomics approach, aiming at global analysis of numerous targeted or non-targeted low molecular compounds (metabolites) in a biological sample, has recently found its application in diverse research areas. A rapid growth of metabolomics has been enabled by substantial advances in analytical techniques such as mass spectrometry (MS) coupled to liquid chromatography (LC) or gas chromatography (GC), and nuclear magnetic resonance (NMR), all the techniques facilitating analysis of a wide range of metabolites with diverse physicochemical properties and occurring at different concentration levels. To process and interpret the complex data obtained within metabolomic-based studies, advanced software algorithms of data handling are needed, consisting of data processing, data pretreatment and data analysis. Data processing proceeds through multiple stages such as filtering, peak detection, deconvolution, alignment and normalization. The need of powerful data-processing methods gave rise to numerous commercial as well as free tools implementing one or several steps of the data processing pipeline. Data pretreatment represents another crucial step that can dramatically change the outcome of the data analysis. This procedure typically involves centering and scaling of the original data to eliminate unwanted systematic bias, while maintaining genuine differences in the examined datasets. Data analysis involves the use of various chemometric tools. Unsupervised pattern recognition techniques (represented mainly by principal component analysis) are often the first step of the data analysis in order to detect patterns in the measured data. On the other hand, supervised pattern recognition techniques (e.g. partial least-squares discriminant analysis, linear discriminant analysis) use the existing information about the class membership of samples to a given group (class or category) to classify a new “unknown” sample using its pattern of measurement. From this point of view, the outputs of metabolomic data analysis may differ depending on the purpose of investigation. In most cases, there is also an interest in identification of the discriminating marker compounds. In this case, the use of a high-resolution instrument enabling to obtain both single MS and MS/MS accurate mass spectra is needed for reliable elemental formula estimation, which is typically followed by a database search. In this presentation, a brief overview of the key steps involved in data handling and interpretation in mass spectrometry-based metabolomics (covering GC–MS, LC–MS and ambient MS instrumental platforms) will be presented. Case studies and practical examples will be used to demonstrate these concepts.

Keywords: Metabolomics, Data handling, GC-MS, LC-MS, Ambient MS

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POSTER SESSION

(P-1 – P-23)

P-1
A NEW TECHNOLOGY DUAL-SBSE-ATD-GC-MS-AMDIS FOR THE STUDY OF THE ENOMETABOLOME OF GRACIANO VITIS VINIFERA VARIETY

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Metabolomics studies rely on the analysis of the multitude of small molecules (metabolites) present in a biological system. Wine consists of a number of metabolites originated either from grapes or even produced during alcoholic and malolactic fermentation by yeast and lactic bacteria respectively. These metabolites are responsible for the wine quality and they constitute its metabolome. The aim of this work was to develop a new analytical technique for the study of the metabolome of Graciano Vitis vinifera wine variety. The Graciano is a singular variety of red grapes, with origin in La Rioja and Navarra (North of Spain) which transfers to the musts an intense red color and aroma, and high acidity. Regarding this variety it has not been reported in literature any data concerning its metabolome. In this sense, the results of this work will provide further knowledge for the characterization of the authenticity of the wine made from this grape variety and it will prevent enological potential fraud. A new technology using Dual-SBSE coupled gas chromatography has been used in order to extract the maximum compounds. In this extraction step, the optimal values for the experimental variables were obtained through the Response Surface Methodology (RSM). In the RSM approach the experimental response (y) is assumed to be a function of the independent variables or factors. Full scan chromatogram data were evaluated by their comparison with Spectral Deconvolution and Identification Automated System (AMDIS) and Mass Hunter deconvolution software tools. As a result, the enometabolome of Graciano Vitis vinifera wine variety was obtained with AMDIS and around 200 metabolites were identified through different databases. These metabolites were grouped into esters, alcohols, acids, nitrogen containing compounds, furans and lactones, ketones, aldehydes, phenols, terpenes and sulfur compounds. The majority of the metabolites found are already reported in literature, however, this work has allowed the identification of new metabolites not referenced in red wines so far. In addition, possible metabolic pathways for these compounds have been suggested.

Keywords: Enometabolome, Graciano, wine, SBSE, deconvolution

Acknowledgement: This work was supported by the Basque Government (Ref: PA1219). The authors would like to thank the Central Service of Analysis of the University of the Basque Country (SGiker) for its excellent technical assistance.

P-2
CAPILLARY ELECTROPHORESIS COUPLED TO MASS SPECTROMETRY FOR THE RAPID EVALUATION OF MARKERS OF FOOD PRODUCTS AND FOOD PROCESSING

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The coupling of capillary electrophoresis to mass spectrometry (CE-MS) has enhanced the potentiality of this separative technique giving to it a new challenge in many fields of analytical chemistry, as demonstrated by many recent papers. We developed and validated new methods for the qualitative and quantitative analysis of selected markers important in the field of food safety, and/or useful for monitoring food technological processing. In this presentation several examples of interesting molecules are reported. Melamine is a nitrogen-rich compound added fraudulently to food to increase the apparent protein content; its toxicity is linked to its reaction with cyanuric acid leading to the formation of insoluble crystals in kidney. We studied the dependence of melamine and cyanuric acid mobility on several parameters, and developed a rapid method for their evaluation in food products. The procedure is also suitable for the control of melamine traces released by cutlery, pointed out by the EFSA alert in 2012. Furosine and hydroxymethylfurfural (HMF) are markers of food processing, largely employed to control thermal treatment and evaluate product quality. HMF is also under investigation for toxicological concern since it was shown to have cytotoxic, genotoxic, and tumoral effects. We optimized and validated a new method for qualitative and quantitative analysis of furosine and HMF in food products by CE coupled to MS-MS. Despite all previous CE methods proposed in literature for furosine analysis, no SPE treatment was required. The method has been applied to the analysis of different food products such pasta, milk, tigelle bread and flour, with particular attention to infant food. Lysozyme is a protein currently used in food technology as additive for its antibacterial activity. It is widely employed in winemaking process to control the growth of lactic bacteria. Since it derives from hen's egg, it is considered a potential allergenic compound, and European Community in 2007 included it in the list of food ingredients that must be specified for safety matter. We developed a method for the analysis of lysozyme in white wines, studying the dependence of its migration on different analytical conditions and testing the stability of the signal obtained. The analytical conditions, including capillary length, background electrolyte concentration and pH, applied voltage, sheath liquid, have been optimized, and the proposed and validated methods have been applied to the quantitative determination of the selected markers in different food products. Our methods can be proposed as powerful analytical tools and valid alternative to LC-MS. In order to test the reliability of our methods, a comparison of some results with data obtained by LC has been carried out. Advantages of CE regards mainly economic impact since few amount of solvent is required, and cheap capillaries are employed instead of dedicated columns whose life is limited.

Keywords: Capillary electrophoresis-mass spectrometry, Melamine, Furosine, HMF, Lysozyme

P-3
ASSESSMENT OF FRUIT JUICE AUTHENTICITY USING UPLC/QTOF MS AND MARKERLYNX DATA EVALUATION

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Adulteration of food and beverages is a growing problem in today's global market. Advanced analytical methods are required to protect the rights of producers and consumers with respect to fraudulent practices, including the adulteration of foods. Fruit juices are particularly susceptible to adulteration, as high value juices are often adulterated with relatively low priced juices, which may also have lower nutritional value. The conventional methods currently used are not able to cover the detection of all possible advanced adulteration techniques. One of the juices commonly targeted for adulteration is pineapple juice, which is widely available throughout the world. Pineapple juice is a relatively high value juice with a reputation for health benefits and it has been used as a remedy for many ailments for centuries. The feasibility of UPLC/QToF MS for assessment of the authenticity of fruit juices (pineapple, orange, apple, grapefruit, and mandarin) was explored. Fruit juice samples were prepared in the laboratory, fresh-pressed, centrifuged, filtered and analysed. Experimental data were processed using an orthogonal partial least squares model (OPLS-DA). Adulteration of pineapple juice with orange, apple and grapefruit juice could be detected at 5% addition level. Using an untargeted approach, MarkerLynx data analysis and hydrophilic interaction liquid chromatography (HILIC) as well as reversed stationary phases, some characteristic markers were detected for each juice. Based on exact mass measurement, elemental composition prediction and mass fragment data analysis, the markers were characterized and identified using mass spectral databases. The applicability of a rapid screening approach using an atmospheric solid phase analysis probe (ASAP) to control fruit juices authenticity was also explored.

Keywords: Authenticity, Pineapple Juice, UPLC, QToF MS, MarkerLynx

P-4
CHANGE OF FLAVONOIDS AS THE DEFENSIVE SUBSTANCE FOR CITRUS FRUIT PEEL AGAINST PENICILLIUM DIGITATUM USING LC-MS/MS: THEIR CONTRIBUTION TO OVERALL ANTIOXIDANT

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A healthy Citrus leiocarpa Hort. ex Tanaka (CLHT), Citrus platymamma Hort. et Tanaka (CPHT) and Citrus nippokoreana Tanaka (CNT) and one infected by Penicillium digitatum were analyzed for flavonoids using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC–MS/MS) in the positive mode with selected ion monitoring (SIM). To investigate the function of the flavonoids as defensive substance, flavonoid content change of the fruit peel inoculated with P. digitatum was monitored by HPLC. The flavonoid concentration in the infected fruit peel decreased initially after infection and then gradually increased before finally progressively decreasing. The antioxidant activity of the flavonoid mixture of the fruit peel was determined via DPPH•, ABTS•+ and reducing power assays.

Keywords: Citrus, flavonoid, defensive substance, HPLC-MS/MS, antioxidant activity

Acknowledgement: This work was supported by a KBSI grant(T32710) to J. S. Jin.

P-5
DIRECT MS-ANALYSIS OF RADIX ANGELICAE SPECIES USING A NEW DIRECT INLET PROBE (DIP)-APCI ION SOURCE

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Ambient ionization techniques allow the direct mass spectrometric analysis of samples in the open atmosphere without the need for sample preparation. In 2005 McEwen and coworkers introduced the atmospheric-pressure solids analysis probe (ASAP). With ASAP volatile or semi-volatile liquid or solid materials are vaporized in the hot nitrogen gas stream from an APCI probe. Ionization then occurs by corona discharge under standard APCI conditions. We developed a new DIP-APCI ion source (DIP = direct inlet probe) which can be connected to an Agilent Technologies 6538 UHD Accurate-Mass Q-TOF and allows the automatic insertion of a liquid or solid sample into the source-region using a temperature-controlled push-rod. This enables us to perform temperature gradients, which permit the separation of sample components according to their boiling point. This approach could be used to minimize ion suppression which is the major drawback of direct mass spectrometric analysis. As part of the development of the new DIP-APCI ion source the influence of the nitrogen flow around the push-rod, of the drying gas flow and of the internal mass calibration by introducing different calibrating solutions was investigated. The linearity and reproducibility of the ionization were tested using caffeine and an extract of Radix Angelica sinensis, respectively. In Chinese Herbal Medicine (CHM) quality control is largely based on the experience of the pharmacist in contrast to western medicine where it is based on Good Manufacturing Practice (GMP). Radix Angelica sinensis (China) is one of the ingredients of Xiao Yao pills that are for example used against irregular menstruation, dizziness and absence of appetite. Due to shortness of Radix Angelica sinensis it is sometimes substituted with other species of the genus Radix Angelicae, for example Radix Angelica gigas (Korea). Our research group uses GCxGC-MS to identify biomarkers in CHM. The GCxGC-MS analyses of different Radix Angelicae species revealed the presence of coumarins in Radix Angelica gigas, but not in Radix Angelica sinensis. Our new DIP-APCI ion source attached to an Agilent Technologies 6538 UHD Accurate-Mass Q-TOF operated in APCI(+)-mode was used to directly analyze the powdered Radix Angelicae samples. The instrument performed the internal mass calibration automatically by introducing a calibrating solution which contains the internal reference masses m/z 121.050873 ($C_5H_4N_4$) and m/z 922.009798 ($C_{18}H_{18}O_6N_3P_3F_{24}$) in methanol. The obtained accurate mass information enabled us to verify the presence of coumarins in Radix Angelica gigas, but not in Radix Angelica sinensis, by direct MS analysis using the DIP-APCI ion source. This demonstrates that the DIP-APCI ion source is a useful tool for a fast quality control for complex samples such as CHM.

Keywords: Mass spectrometry, DIP-APCI, chinese herbal medicine (CHM)

P-6
RAPID DETERMINATION OF THE MAIN PHYTOSTEROLS IN RED WINE BY UPLC-MS USING ATMOSPHERIC PRESSURE CHEMICAL INTERFACE

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Phytosterols and phytostanols have a chemical structure similar to cholesterol but are only available to humans through plant foods such as seeds, cereals, fruits, and vegetable or industrial supplements from plant origin. More than 100 types of these compounds have been reported in plant species. 4-Demethylsterols such as sitosterol, campesterol, and stigmasterol are the most abundant sterols in plants. To date, there is no relevant data about the sterol content in red wine in the revised literature. The objective of this study is the identification of phytosterols and phytostanols and the developement of an analytical method allowing the quantification of the above compounds in wine. The application of UPLC-APCI/MS to sterols characterization is a useful tool and was selected to perform the present study. The optimal conditions for the separation of sterols were achieved using a C18 column (2.1 x 30mm, 3.5µm) with a mobile phase consists of water-methanol under gradient conditions, giving a run time below 5 min. Most common methods for extraction of sterol and stanol lipid composition involve nonpolar solvents for liquid-liquid extraction such as hexane, cloroform-methanol, methylene chloride, ethyle acetate or acetone. However, in plant tissues phytosterols occur as free sterols, steryl esters (SE), steryl glucosides (SG) and acylated steryl glucosides (ASG). For this reason, an acid or alkaline hydrolysis of phytosterol conjugates was carried out, after extraction step, to transform in free sterols. A rapid and sensitive method has been developed for extraction, identification and quantification of desmosterol, ergosterol, cholesterol, brassicasterol, campesterol, fucosterol, stigmasterol, ß-sitosterol and sitostanol in different varieties of red wine samples.

Keywords: Phytosterols, phytostanols, red wine, UPLC, APCI-MS

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P-7
MULTICLASS DETERMINATION OF VETERINARY DRUGS RESIDUES IN ANIMAL PRODUCTS USING LC-MS/MS

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A large number of antibacterial drugs are available for veterinary use in food-producing animals. Veterinary Drugs are widely used for the treatment and prevention of disease in livestock. Inadequate use of these drugs can lead health problems. In order to ensure human food safety, European Union (EU) has set Maximum Residues Limits (MRL) for most of them in different matrices (muscle, milk. eggs …) since the MRL for these molecules are often pretty low. For the analysis of veterinary drug residues sensitive analytical methods are needed. Most of the former published methods contain time consuming, SPE clean up procedures and analyse only few different classes or compounds. In food control of veterinary drug residues, screening methods based on microbiological assays are mainly employed but they present low specificity and suspected samples need further analysis to confirm the results. A new and modern approach for multi-screening analysis is the use of LC/MSMS technique. In this work we present a multi-class, multi-residue method using Liquid chromatografy couplet with Electrospray Ionization Tandem Mass Spectrometry for the determination of about 60 veterinary drugs in animal products (meat, eggs, milk…) with a simple and rapid sample preparation procedure. The method has been developed for five different antibiotic classes covering Tetracyclines, Quinolones, Macrolides, Sulfonamides and ß-Lactams and it has been validated for an extended number of matrices. In conclusion, this method is less time consuming, inexpensive and allow the simultaneus detection of more than 60 veterinary drugs. Morover, our results demostrate that this screening method is able to detect target compounds at level ≤ MRL and very high specificity.

Keywords: LC-MS/MS, veterinary drugs, multi-residue method

P-8
STATINS AS ENVIRONMENTAL POLLUTANS IN WASTEWATER TREATMENT PLANT EFFLUENT IN NORTH SARDINIA

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Wastewater treatment plant (WWTP) effluents can be, one of the sources of pharmaceutical and personal care products (PPCP) into streams and rivers. The aims of this study were to study the presence of these emerging contaminants and to develop a LC-MS method for their determination and quantification. Water samples from different treatment plants were analyzed for cholesterol-lowering drug (Simvastatin, Rosuvastatin, Atorvastatin), using enrichment of analytes with SPE clean up and High-performance liquid chromatography coupled with electrospray ionization ion-trap tandem mass spectrometry. Atorvastatin was detected in effluent of WWTP. Despite of frequent use, the fate and effects of statins in environment are largely unknown and althought some of these compounds can be degraded in the environment, it is assumed that they could be as persistent compounds due to their regular infusion via WWTP effluent. Statins could be considered as markers of human pollution, according to the cholesterol-lowering drug data consumption in north Sardinia, due to genetic hypercholesterolemia of the population.

Keywords: Pollution, PPCP, LCMS

P-9
ANALYSIS OF MYCOTOXINS IN BARLEY USING UHPLC-HRMS: COMPARISON OF EFFICIENCY AND EFFICACY OF DIFFERENT EXTRACTION PROCEDURES

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The effectiveness of four extraction methods (modified QuEChERS, matrix solid-phase dispersion (MSPD), solid-liquid extraction (SLE) and solid-phase extraction (SPE) clean-up) were evaluated for simultaneous determination of 32 mycotoxins produced by the genus Fusarium, Claviceps, Aspergillus, Penicillium and Alternaria in barley by ultra high pressure liquid chromatography coupled to ultra-high resolution mass spectrometry (UHPLC-Orbitrap® MS). The efficiency and efficacy of extraction methods were evaluated and compared in number of mycotoxins extracted and recoveries obtained. From the one point of view, QuEChERS procedure was fast and easy, as well as it was able to successfully extract all selected mycotoxins. On the other hand, the SLE method, MSPD and SPE clean-up method did not extract adequately all selected mycotoxins recoveries were not suitable enough. Thereby, method employing QuEChERS extraction connected with UHPLC-Orbitrap® MS was validated and recoveries ranged from 72 to 101% for selected mycotoxins with only one exception nivalenol (NIV) and deoxynivalenol-3-glucoside (D3G), which were lower than 67%. Relative standard deviations (RSD) were lower than 17.4% for all target mycotoxins. The lowest calibration levels (LCLs) ranged from 1 to 100 µg/kg. Validated method was finally used for monitoring mycotoxins in Czech barley samples: only Fusarium toxins were detected in 53% of samples. Mycotoxins with high incidence were enniatins.

Keywords: QuEChERS, MSPD, Clean-up, Solid-liquid extraction, Mycotoxins, Orbitrap

Acknowledgement: J.R. thanks to Spanish Ministry of Education for a "short-term" visit grant.

P-10
OPTIMIZATION OF HEADSPACE IN-TUBE EXTRACTION GAS-CHROMATOGRAPHY MASS SPECTROMETRY METHOD FOR THE ANALYSIS OF SEA BUCKTHORN VOLATILE PROFILE

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Headspace In-Tube Extraction Gas-Chromatography Mass Spectrometry (HS-ITEX/GC-MS) is a modern technique for the extraction and analysis of volatile aroma compunds. In the case of ITEX technique, the release of volatile compounds is achieved by incubating the headspace vial containing the sample at an appropriate temperature for a certain period of time. The volatile and semi-volatile compounds from the gaseous phase are then adsorbed in a microtrap, followed by their transfer to the GC-MS system for separation and identification. The purpose of the study was to optimize the extraction and separation parameters of HS-ITEX/GC-MS technique, so that it can be used for sea buckthorn varieties discrimination, based on their volatile aroma profile. The optimized parameters were: incubation temperature (35°C and 60°C), incubation time (20 and 30 min.), number of extraction strokes (30, 40), sample weight (2g, 3g) and column temperature program (five programs were tested). The analyses were carried out on a GCMS QP-2010 (Schimadzu) model gas chromatograph – mass spectrometer equipped with a CombiPAL AOC-5000 autosampler. The volatile aroma compounds were separated on a Zebron ZB-5ms capillary column of 50 m × 0.32 mm i.d and 0.25 µm film thickness. The carrier gas was helium, the ion source temperature and interface temperature were set at 250°C and the MS mode was EI. The mass range scanned was 40-350u. The identification of separated compounds was made based on the comparison of the obtained mass spectra with the ones from the mass spectra libraries, NIST27 and NIST147. The main volatile compounds found in sea buckthorn samples were esters of branched or normal chain aliphatic alcohols and acids, such as: 3-methylbutanoic acid ethyl ester, 2-methylbutanoic acid ethyl ester, 3-methylbutyl 3-methylbutanoate, hexanoic acid ethyl ester, octanoic acid ethyl ester, benzoic acid ethyl ester. The proportion of these major compounds was over 70% of total peak area. Other compounds identified in the analyzed samples were alcohols (3-methyl-1-butanol, 1-hexanol), aldehydes (hexanal, heptanal, octanal, benzaldehyde), ketones (6-methyl-5-hepten-2-one, acetophenone) or terpenes (limonene, beta-trans-ocimene). The optimized method is a simple, efficient and low time consuming method that can be successfully used for volatile aroma compounds extraction and discrimination of Romanian sea buckthorn varieties.

Keywords: ITEX/GC-MS, optimization, volatiles, sea buckthorn

Acknowledgement: This work was financially supported by the European Social Fund - The Operational Sectorial Program for Human Resource Development 2007–2013, project – Cellular and molecular biotechnologies for medical applications – FSE POSDRU/89/1.5/S/60746 and by Project PNCD II Ideeas, 2011–2014: Effect of esterification on the stability and antioxidant capacity of xanthophylls – from model systems to food systems, contract no. 276/5.10.2011

P-11
DETECTION OF MYCOTOXINS AND ITS METABOLITES IN HUMAN MILK USING ORBITRAP TECHNOLOGY

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The occurrence of mycotoxins in human milk is one of the most serious problems of food hygiene, since milk is the unique nutrient for infants. This population is extremely vulnerable because their diet is not varied and depends on mother dietary habits. It has been reported that in human milk a variable amount of mycotoxins, ingested by the mother, can be accumulated as intact or metabolized. Despite the constantly claimed need of frequent surveys on a so delicate public health issue, few studies are available worldwide. The aim of the present study was to monitor the presence of 25 target mycotoxins and to screen the presence of its possible metabolites and conjugate mycotoxins. With this objective, 20 samples of human milk were collected at Spanish milk bank during 2011. To extract mycotoxins from milk a QuEChERS extraction method was validated using 10 ml of milk sample and 10 ml of acetonitrile. After salts use and centrifugation, 1 ml of the organic aliquot was analysed. Results demonstrated that the developed QuEChERS extraction by UHPLC-HRMS detection fulfilled the recovery and repeatability criteria established by the Commission Regulation 2002/657/EC for the target mycotoxins. Moreover, Orbitrap MS instrument permitted the screening of target and non-target mycotoxins, which standards are not available, in a retrospective data analysis by ultra high resolution mass spectrometry.

Keywords: Mycotoxins, human milk, QuEChERS, Orbitrap

Acknowledgement: Spanish Ministry of Science and Innovation (AGL2010-17024/ALI)

P-12
TRACING THE GEOGRAPHICAL ORIGIN OF AUSTRALIAN, CANADIAN, USA AND JAPANESE WHEAT FLOUR USING STABLE CARBON, NITROGEN AND OXYGEN ISOTOPE ANALYSIS

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The food industry has been expanding globally, and consumers can obtain various food products from all over the world. This circulation requires a valid traceability system to ensure the safety and high quality of food. In Japan, the Japanese Agricultural Standard (JAS) Law was introduced in 1950 to prevent food frauds such as mislabeling and adulteration. In accordance with this law, packaged wheat flour is required to be labeled to indicate its cultivation area. However, it is extremely probable that packages are incorrectly labeled, either accidentally or intentionally. Thus, there is a requirement for a simple analytical method for checking the authenticity of wheat flour. Recently, characterization of isotopic composition of food materials has been used to prevent illegal mislabeling and adulteration. For example, adulterated honey and juice products and the geographical origin of meat, dairy products, wine, and cereal crops can be traced by using natural differences in their carbon, nitrogen, and/or oxygen isotopic compositions. In this study, we determined stable carbon, nitrogen and oxygen isotope ratios of wheat flour from various cultivated areas in Australia, Canada, USA and Japan to discriminate their geographical origin. Of 58 samples, 15 were from Australia, 17 were from Canada and USA, and 26 were from Japan. Stable carbon, nitrogen and oxygen isotope ratios were determined by using elemental analyzer/isotope ratio mass spectrometry (EA/IRMS). The ƒÂ13C values of Australian (−23.6‰ to −20.7‰), Canadian (−23.8‰ to −22.0‰), and USA (−23.9‰ to −23.4‰) wheat flour higher than those of Japanese wheat flour (−27.1‰ to −25.1‰) (P<0.001). The carbon isotopic composition of plant materials depends on the water stress such as the amount of precipitation. The Australian wheat samples are higher ƒÂ18O values (+29.5‰ to +35.9‰) than Canadian (+23.2‰ to +25.6‰), USA (+25.0‰ to +27.2‰) and Japanese samples (+20.2‰ to +31.6‰) (P<0.001). In general, oxygen isotopic composition of plant materials mainly reflects that of precipitation, which depends on latitude and altitudes. Based on the weighted annual ƒÂ18O values in the GNIP/ISOHIS database from International Atomic Energy Agency (IAEA), the ƒÂ18O value of precipitation in New South Wales (Australia) is actually higher than that in Japan and the northern USA states. In Japanese samples, the wheat samples from Hokkaido have lowest ƒÂ18O values. Hokkaido is the most northern prefecture in Japan and the ƒÂ18O values of its precipitation are relatively lower in Japan. These results suggest that the ƒÂ18O values of the wheat samples can be representative of the growth environments. Thus, stable isotope analysis would be potentially useful for trace the geographical origin of Australian, Canadian, USA and Japanese wheat samples.

Keywords: Geographical origin, stable isotope analysis, wheat flour

Acknowledgement: This work was supported by a research grant from the Elizabeth Arnold Fuji Foundation in 2011.

P-13
STUDY OF FATTY ACID PROFILES IN THREE NATIVE OLIVE CULTIVARS FROM ALBANIA

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Recent data reveal that the annual production has reached to 11 000 tons of olive oil, in Albania. This study characterizes the fatty acid profiles of monovarietal olive oils from 3 olive varieties, namely: Kamza, Ulli i bardhe Tirana, Nisiot, all from the same harvesting period. Results on fatty acid (FA) profiles exhibit a great variation in oleic acid, from 64.71 ± 0.12% (Nisiot) to 80.32 ± 0.21% (Kamza), values which are within the normal range for such FA. The content of linoleic acid varies from 4.08 ± 0.04% (Kamza) to 13.24 ± 0.01% (Nisiot), whereas the content of linolenic acid varies from 0.48 ± 0.01% (Ulliri Bardhe Tirana) to 0.80 ± 0.05% (Kamza). Three olive varieties revealed moderate levels of palmitic acid, which varied between 9.27 ± 0.05% (Kamza) to 15.22 ± 0.02% (Nisiot). From a nutritional point of view, it is worth noticing that the Kamza variety has an n-6/n-3 ratio of 5.07, while the Ulliri bardhë Tirana goes to 14.41. The potential oxidative stability was studied through evaluation of 18:1/18:2. Two olive varieties produced monovarietal olive oils of good stability 19.69 (Kamza) and 10.82 (Ulliri bardhë Tirana), while the Nisiot cultivar resulted under 7.00.

Keywords: Kamza, Ulliri bardhë Tirana, Nisiot, Fatty Acids, Stability Index

Acknowledgement: University of Tirana, Faculty of Natural Sciences

P-14
ESI-LC-MS/MS METABOLIC PROFILING OF PHENOLIC ACIDS IN URINE OF HUMAN VOLUNTEERS AFTER CONSUMPTION OF LONICERA CAERULEA FRUIT

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Lonicera caerulea berries are a rich source of dietary anthocyanins and phenolic acids. However, their bioavailability is limited. The polyphenols reach the colon and are transformed by intestinal microflora into simpler phenolics. Apart from this, there is insufficient information on excreted metabolites in urine. This study is focused on the MS-based screening of the biotransformation products, benzoic and cinnamic acid hydroxyderivatives, in urine of healthy human volunteers after ingestion of Lonicera caerulea fruits. The subjects (n=10) consumed 165 g fresh fruit (208 mg of anthocyanins) per day for one week. In urine samples collected on day 0 and day 7, before and after ingestion of berries, 18 phenolic acids, in the free form and/or as conjugated metabolites, were identified and determined by the ESI-LC-MS/MS method. On day 7, the levels of benzoic, protocatechuic, vanillic, 3-hydroxycinnamic, p-coumaric, isoferulic, ferulic and hippuric acids were significantly increased over day 0 ($p<0.05$). The level of 4-hydroxybenzoic, phenylacetic, 2-hydroxyphenylacetic, 3-hydroxyphenylacetic, 4-hydroxyphenylacetic, 3,4-dihydroxyphenylacetic, homovanillic, dihydrocaffeic, dihydroferulic and 2-hydroxyhippuric acid was practically the same as on day 0. The concentration of anthocyanins in urine samples was under the limit of detection. The methodology and pilot results presented here are a fundamental step towards effective future metabolic studies of polyphenols in human.

Keywords: Lonicera caerulea, phenolics, urine, determination of metabolites

Acknowledgement: This work was supported by the Grant LF_2012_010.

P-15
CHARACTERIZATION OF NATURAL PRODUCTS WITH A MODIFIED AMBIENT SOURCE USING A MESH SCREEN SAMPLING CARD

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Ambient ionization techniques rely on the ability to place a sample directly in the path of the ionization beam. A less expensive device has been developed that allows samples to be placed on a metal mesh screen attached to a simple sampling card. This requires some, but often minimal sample preparation. The device has been examined to determine its potential for the characterization of natural substances using a QTOF mass spectrometer. Standards in methanol solutions of flavonoids, ginkgolides, catechins, and ginosenosides where analyzed along with extracts of green tea, a ginseng supplement, and a Ginkgo Biloba supplement. Different sample preparations were evaluated and are discussed. Results shows that many of these standards such as catichins, quercetin, and ginkolides can be detected using this device. However, the steroid glycosides found in ginseng did not ionize well and were not detected. Identification was facilitated using accurate mass measurement and MS/MS. In addition, there were unidentified ions detected in the natural products that could facilitate characterization. Both accurate MS and MS/MS could be advantageous for identification of the unknown compounds. This work examines the advantages and disadvantages of this unique ambient MS source. In addition, the use of reference ions to attain accurate mass measurement for MS with better than 2 ppm accuracy and MS/MS with better than 5 ppm mass accuracy is described.

Keywords: Green tea, ginseng, ginkgo biloba, QTOF MS

Acknowledgement: Joseph Tice, Jordan Krechmer, and Brian Musselman of Ionsense; and Mark Werlich and Bruce Wang of Agilent

P-16
USING OF DART-MS TECHNIQUE FOR STUDY OF COD LIVER OIL SUPPLEMENT STABILITY

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Fish oil and cod liver oil are popular naturally-derived nutritional supplements. They are rich in essential omega-3 fatty acids, represented mainly by biologically active polyunsaturated acids like eicosapentaenic acid (EPA) and docosahexaenic acid (DHA). These polyunsaturated fatty acids (PUFAs) cannot be synthesized in human body, and therefore, they need to be consumed as part of a diet, or through respective supplements.
However, PUFAs are susceptible to oxidative spoilage, in the presence of air oxygen, radical reaction - autooxidation reaction takes place. In the first step hydroperoxides are formed, and subsequently, oxo-, hydroxy- and epoxy- acids (with both the same or shorter chain). Hydroperoxides of PUFAs formed by autoxidation are very unstable and break down into a wide variety of volatile sensorically active compounds as well as nonvolatile products.
The aim of this study was to monitor potential oxidative changes in fish oil used in food supplements by means of non-target fingerprinting strategy. For this purpose, ambient mass spectrometry technique employing Direct Analysis in Real Time (DART) ion source coupled with High Resolution Mass Spectrometer (HR-MS) with orbitrap mass analyzer was used. The effect of both heating and long-term storage of cod liver oil as well as the effect of antioxidant addition was well documented by this technique. Markers of oxidation products were found especially in heated oil, and, at the same time, a relative decrease of PUFAs was observed.

Keywords: Cod liver oil, food supplement, metabolomic profiling, DART-MS

Acknowledgement: This study was carried out with support from the Ministry of Education, Youth and Sports, Czech Republic, the project MSM 6046137305 and specific university research (MSMT no. 21/2012).

P-17
METABOLOMIC FINGERPRINTING/PROFILING EMPLOYING DART COUPLED WITH TOF-MS AND ORBITRAP-MS FOR DGGS AUTHENTICITY AND TRACEABILITY

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Distillers dried grains with solubles (DDGS) are the by-products from bio-ethanol production which have high protein content and are therefore very valuable in feeding livestock at a low price level. Determining a geographical origin is of particular interest with regards to co-products from bio-ethanol production. The reason is that the financial rewards lie mainly in the production of fuel, whereas feed materials derived from processing waste materials will be less well controlled.
In this study, the methods based on metabolomic fingerprinting/profiling for authenticity and traceability of samples originating from different countries (USA, China, Germany) were evaluated. For extraction, aqueous methanol and cyclohexane were chosen as the best solvents to obtain a broad spectrum of polar and nonpolar metabolites, respectively. Instrumental analyses were performed using ambient mass spectrometry [Direct Analysis in Real Time (DART) ion source coupled with both Time-of-Flight (TOF) and Orbitrap mass spectrometer]. In addition to metabolomic fingerprinting, identification of some markers has been conducted. In an organic fraction, triacylglycerols were the main group of identified analytes, while in an aqueous fraction, predominantly organic acids, amino acids and sugars were identified. Samples were classified using sophisticated chemometric tools.

Keywords: Metabolomic fingerprinting/profiling, DDGS, DART-MS, authenticity, traceability, chemometrics

Acknowledgement: The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°265702.

P-18
AMBIENT MASS SPECTROMETRY AS A NEW TOOL FOR THE CHARACTERIZATION OF LIPIDIC FRACTION OF DIFFERENT KINDS OF FISH

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This study was realized within the FP7 EU project CONffIDENCE, which is focused on the development of fast and simple methods for analysis of various groups of compounds in the food and feed. In this part of project the application of a new innovative analytical method based on direct analysis in real time (DART) for characterization of samples of fish mainly of lipid fraction, mainly of triglycerides and fatty acids, was tested. The main advantages of this technique is very rapid measurement, one sample could be measured in several second. Typically the polar fraction of lipids represented by free fatty acids is isolated into polar solvent (water or methanol) and the non-polar fraction represented by triacylglycerols isolated from the sample by hexane. Among others, the DART technique allows to obtain the characteristic metabolomic profiles, resulting in the possible identification, authentication of each species.

In this case, when the lipid fraction of fish was analysed we tried to test the extract which was obtained within the analysis of persistent organic pollutants. In this approach fish tissue was homogenized, water and ethyl acetate was added and after addition of inorganic salts sample was shaken and centrifuged and after that analysed using DART-MS. In this study, ambient mass spectrometry based on DART ion source coupled with high resolution (Orbitrap) mass spectrometer was employed. The same extract could be used for characterization both non-polar compounds mainly represented by triacylglycerols and polar compounds mainly represented by free fatty acids. To process complex generated data (mass spectra of polar and non-polar fraction) advanced chemometric tools had to be employed.

The results will contribute to the complexity of information obtained from analyses of fish samples and the overall characterization of samples of fish. The data will be further processed, compared and correlated with other obtained data, such as information about contaminants in fish..

Keywords: Authenticity, DART, fish, profiling, fingerprinting

Acknowledgement: This research was supported by the European research project CONffIDENCE (FP7-211326-CP) "Contaminants in food and feed: Inexpensive detection for control of exposure" which is a part of Seventh framework program.

P-19
MYCOTOXINS IN FOOD SUPPLEMENTS

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Production strategy for quality food and effect control of food composition are one of the main themes in internacional food research. A number of scientific publications illustrates the relationship among the composition, the amount of food intake and population health. However, the importance of natural dietary supplements is increasingly discussed, because food supplements are gaining in high popularity among consumers recently. However, natural food supplements based on plant extracts may contain various natural toxins potentially, in addition to various health-promoting substances such as vitamins, minerals and antioxidants. This study was focused on problems possible mycotoxin presence in natural food supplements based on a medical plant Milk thistle (Silybum marianum) specifically. Antioxidant substances, containing in this plant (silymarin), are widely known for its positive detoxifying effects on liver cells especially. However, mycotoxins, toxic secondary metabolites of microscopic filamentous fungi, are knowed their hepatotoxic effects. 21 samples of dietary supplements available on the Czech market were investigated for presence 53 mycotoxins (Fusarium, Alternaria, Penicillium, Aspergillus, Claviceps, and others). For mycotoxins isolation, QuEChERS-based method was used, for identification and quantification, ultra-high performance liquid chromatogrphy coupled with tandem mass spectrometry (U-HPLC-MS/MS) was enabled. In almost all analyzed samples were detected to a lesser or greater content of Fusarium and / or Alternarium mycotoxins. The mycotoxins, which are the European Food Safety Authority (EFSA) set down the value of tolerable daily intake (TDI), were recalculated toxine amount in the maximum daily intake of the supplement to the percentage of TDI. For some analyzed samples was contain of mycotoxins taken up to several tens % TDI.

Keywords: Supplements, mycotoxins, LC-MS

Acknowledgement: Finacial support from specific university research (MSMT No 21/2012)

P-20
QUANTITATIVE ANALYSIS OF CARBENDAZIM AND OTHER PESTICIDES IN FRUIT JUICES BY DIRECT ANALYSIS IN REAL TIME (DART) MASS SPECTROMETRY

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Routine pesticide and fungicide use in the United States, as well as abroad warrants the need for analytical techniques that can rapidly screen and quantify residues in order to efficiently monitor produce products before reaching the consumer market. The allowable residue levels of chemical residues including pesticides and fungicides on produce are governed by the US EPA Code of Federal Regulations that sets tolerance levels based on the commodity. Of particular interest in the United States, carbendazim was found in imported orange juice and orange juice concentrates from Brazil, where the use of that fungicide is legal and therefore rapid product screening would increase consumer safety in the US and worldwide. The Direct Analysis in Real Time (DART) ambient ionization technique offers the ability to rapidly screen the surface of produce for pesticides by a direct swabbing method and permits direct analysis of fruit juices in seconds. With automated sample introduction rapid screening and quantitative measurements can be completed using DART ionization coupled to high resolution accurate mass and triple quadrupole mass spectrometers. Limits of detection using the DART ionization quantitative method coupled with Q Exactive and API 4000 QTRAP mass spectrometers were below 10 ppb for a 10 pesticide mixture detected in a variety of fruit juices, as well as for carbendazim directly analyzed from fruit juices. A number of the orange juices from the EU (5 juices), India (4 juices) and USA (3 juices) were screened for carbendazim and three juices all purchased in the EU tested positive for the fungicide at levels ranging from < 5 ppb up to 21 ppb.

Keywords: Pesticides, Fruit Juices, DART-MS, Quantitation

AUTHOR – INDEX

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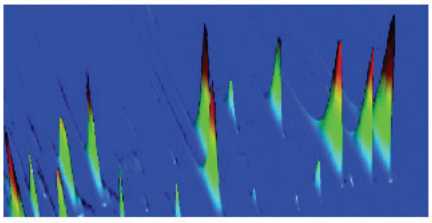

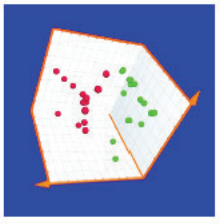

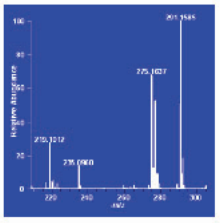

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