Optimizing a 190+ Pesticides Multi-Residue Screening Workflow for the Preparation and Analysis of Produce by LC-MS/MS

Joseph Konschnik, Landon A Wiest, Dan Li, Alexacndria M Pavkovich, Sue Steinike, and Justin Steimling

Corresponding Author
Joseph Konschnik, joe.konschnik@restek.com
RESTEK Corporation

Abstract
Pesticides are ubiquitously used to help increase crop yields; however, they can pose risks for public health and pollinators (honeybees). Faster multi-residue screening workflows, which combine easier sample preparation techniques that yield higher recoveries with lower instrument detection limits in fruits and vegetables, are often sought. Accomplishing these goals increases sample throughput, and reduces costs for laboratories and their clients. To demonstrate the feasibility of developing improved methods, organic celery and other representative matrices were spiked with pesticides down to 10 ppb. Samples were extracted using Restek QuEChERS Slim Pouch salts, and cleaned up with complementary dSPE. Each sample was diluted 10x with water prior to analysis. Separations were performed with a Restek Raptor ARC-18 column (100 mm x 2.1 mm, 2.7 µm) on a Shimadzu Nexera UHPLC. A Shimadzu LCMS-8060 was used for detection. Recovery and precision results from organic celery, spinach, avocado, orange, brown rice flour and honey will be shown.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-01

Coauthors
Landon A Wiest, RESTEK Corporation
Dan Li, RESTEK Corporation
Alexacndria M Pavkovich, RESTEK Corporation
Sue Steinike, RESTEK Corporation
Justin Steimling, RESTEK Corporation

Developing a robust LC-MS/MS method for the determination of anionic polar pesticides in a range of foodstuffs without derivatization

Emily Britton, Joe Romano, Dimple Shah, Benjamin Wuyts, and Euan Ross

Corresponding Author
Emily Britton, emily_britton@waters.com
Waters

Abstract
Glyphosate continues to cause controversy and so analysis is of considerable interest to governments, the food industry and contract testing laboratories. Many wish to move away from methodology that employs derivatization to save time and expand the scope to cover other polar and ionic pesticides. Chromatographic retention and separation were optimized using a novel hydrophilic interaction liquid chromatography (HILIC) column, applying an acidified mobile phase gradient, with and without ammonium formate. The performance of a buffered and un-buffered version of the method was compared. Removal of the ammonium formate from the mobile phase resulted in improved sensitivity without compromising chromatographic performance. The aim was to achieve chromatographic retention and baseline separation of isobaric compounds whilst providing maximum sensitivity of all target analytes. Foods of plant origin were prepared using a modified version of the Quick Polar Pesticides (QuPPe) extraction procedure and spiked with a panel of representative anionic polar pesticides for analysis. All analytes were sufficiently detected at concentrations <0.01 mg/kg in matrix-matched standards using the new acidified method. All isobaric pairs (AMPA/fosetyl al and fosetyl al/phosphonic acid) were well separated. The performance was assessed using the relevant criteria defined in the SANTE guidance document (SANTE/11813/2017). Linearity was assessed through matrix-matched calibration over a suitable concentration range (0.001-0.1 mg/kg). Ion ratios and retention times agreed well with reference values and all were within the required tolerances (±30 % and ±0.1 minutes, respectively).

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-02

Coauthors
Joe Romano, Waters
Dimple Shah, waters
Benjamin Wuyts, Waters
Euan Ross, Waters

Detection of Pesticides and Herbicides in Craft Beer Using DART-MS

Frederick Liu, Brittany Laramee, Taylor Feraco, Paul Liang, and Brian Musselman

Corresponding Author
Frederick Liu, li@ionsense.com
Ionsense, Inc.

Abstract
The plants that produce the main agricultural ingredients used in the crafting of beer, such as barley and hops, are often treated with pesticides to reach good yields and reduce the losses during storage by protecting the plants from insects and pests. Herbicides are also used to protect the plants from weeds. One herbicide, glyphosate, which is a known carcinogen, has been recently found in 14 beers, which included beers from major brands like Budweiser, Guinness, Samuel Adams, etc. These pesticides and herbicide agrochemicals can persist in the plants for a long time and could be carried over to the beer from raw materials, malt and hops. As a result, it is important to be able to detect pesticide and herbicide residues in the finished beers. Here we describe a high throughput analytical method that employs Direct Analysis in Real Time combined with mass spectrometry (DART-MS) for detecting pesticides in beer. Craft beers are spiked with various concentrations of glyphosate and pesticides such as azoxystrobin, flonicamid, metalaxyl, and imidacloprid to simulate finished beer containing pesticides. Beers are sampled using a liquid handling robot and deposited on a wire mesh consumable for automated analysis by DART-MS. Limit of detection is determined for each pesticide. Chemometric models are created and employed to determine beers that contain trace amounts of pesticides. These beers containing pesticides are then searched against our DART-MS library database to identify the specific pesticides. This method can be potentially used to monitor pesticides in finished beer products.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-03

Coauthors
Brittany Laramee, Ionsense, Inc.
Taylor Feraco, NeXeP LLC.
Paul Liang, Ionsense, Inc.
Brian Musselman, Ionsense, Inc.

The analysis of polar anionic pesticides and contaminants by a new single, multi-analyte, robust and sensitive 'sample-to result' IC-MS/MS workflow

Dan Quinn, Fausto Pigozzo, Richard Fussell, and Qilei Guo

Corresponding Author
Dan Quinn, daniel.quinn@thermofisher.com
Thermo Fisher Scientific

Abstract
The introduction of the commonly used Quick Polar Pesticides (QuPPe) Method was a major step forward, but it is still analytically challenging almost 10 years later. The absence of a liquid partitioning and/or solid phase clean-up steps result in high concentrations of matrix co-extractives. This IC-MS/MS workflow addresses this issue with high capacity ion exchange columns that withstand higher sample loading enabling improved detection limits for polar analytes in difficult matrices, such as cereals and cereal products. This poster describes the development and validation of a new integrated 'sample to results' workflow for a reliable and sensitive quantitation of polar anionic pesticides in food. The workflow uses a high capacity ion exchange column with post column eluent suppression coupled to a high sensitivity triple quadrupole mass spectrometer (IC-MS/MS). This development is important because polar anionic pesticides and contaminants such as glyphosate, perchlorate, chlorate and the like, often occur as residues in food, but are not always analyzed because they are not 'amenable' to generic multi-analyte methods. Samples were extracted based on a modification of the QuPPe Method. Wheat flour were hydrated and extracted with methanol. The extract was placed in a freezer for 15 mins, then centrifuged (8000 rpm for 8 mins) and supernatant passed through a Dionex™ OnGuard™ II RP cartridge. Finally, the extract was filtered using a Thermo Scientific™ Nalgene™ 25 mm syringe filter, PES, 0.2 µm followed by 10x dilution with deionized water for injection. The instrument and separation components include; a Dionex™ Integrion™ HPIC™ system with an electrolytic eluent generator and conductivity cell coupled to a Thermo Scientific™ Dionex™ AS-AP Autosampler and Thermo Scientific™ TSQ Altis™ Triple Quadrupole Mass Spectrometer. Separation was achieved using a Thermo Scientific™ Dionex™ IonPac™ AS19-4µm Guard, 2 × 50 mm coupled to a Thermo Scientific™ Dionex™ IonPac™ AS19-4µm Analytical, 2 × 250 mm column with elution of polar anionic analytes using a potassium hydroxide gradient. The injection volume was 25 µL. A total of 15 anionic polar pesticides in a single method were validated in wheat flour. The linear dynamic range was excellent over the range tested, 4-200 ng/g. The matrix-matched calibration approach with internal standards (MMS+LIS), and the matrix-extracted calibration (MES) approach without internal standards produced equivalent results for wheat flour and improved results compared to matrix-matched calibration without internal standards. Using MES, the recoveries were in the range 80-100 % with a repeatability <15%, for chlorate, perchlorate, glufosinate, N-acetyl glufosinate, 3-MPPA, glyphosate, AMPA, N-acetyl AMPA, Fosetyl-Al, phosphonic acid, ethephon, HEPA and more, in a single analysis. Furthermore MS/MS ion ratios, retention time stability, recovery and precision data met the EU SANTE/11813/2017 method performance criteria. The results demonstrate that a workflow based on IC-MS/MS will overcome many of the issues experienced with previous methods reported for the analysis of polar pesticides and provides confidence in results by full compliance with the EU SANTE guidelines.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-04

Coauthors
Fausto Pigozzo, Thermo Fisher Scientific
Richard Fussell, Thermo Fisher Scientific
Qilei Guo, Thermo Fisher Scientific

A Multiresidue Method for Pesticide Analysis Using an Orbitrap Tribrid Mass Spectrometer and Automatic Background Exclusion

Dan Quinn, Dipankar Ghosh, Anastasia Kalli, and Seema Sharma

Corresponding Author
Dan Quinn, daniel.quinn@thermofisher.com
Thermo Fisher Scientific

Abstract
Pesticides are routinely applied to crops for preventing, destroying or controlling pest activity. In order to protect the consumers and ensure they are not being exposed to pesticide levels harmful for their health, pesticides are regulated and several countries have established maximum residue levels (MRLs). Given the large number of pesticides used and the globalization of the food industry, multiresidue methods offer a great advantage allowing analysis of hundreds of pesticides in a single run. We have implemented a multiresidue method for the analysis of 250 pesticides on a Thermo Scientific™Orbitrap ID-X™ Tribrid™ mass spectrometer utilizing an automatic background extraction workflow (AcquireX). Detection limits were below MRLs and the background extraction workflow provided improved pesticide screening and confirmation at lower concentration levels. Organic and non-organic strawberry samples were obtained from a local retail store. Following homogenization, strawberry samples were extracted using a QuEChERS extraction kit. Briefly 10 g of sample was weighed into the QuEChERS extraction tube and 10ml of ACN was added. Samples were shaken, centrifuged and the supernatant was collected. The matrix extracts were spiked with the pesticide standards (250 pesticides) at different concentration levels ranging from 0.05 to 200 ppb. Injection sample volume was 1 ul. Chromatographic separation was performed on a Vanquish UHPLC system using an Accucore aQ column. Mass spectrometric analysis was performed on an Orbitrap ID-X Tribrid mass spectrometer using AcquireX workflow, for automated generation of background exclusion list, or data dependent acquisition (DDA). We have evaluated the performance of a multi-residue pesticide method utilizing high mass accuracy and high resolution for semi-quantitation and screening of pesticide residues in a strawberry matrix. Pesticide quantitation was performed in full MS scan mode followed by MS/MS for confirmation and screening. For pesticides screening and confirmation data dependent acquisition (DDA) and AcquireX were tested. Data analysis was performed with Trace Finder software with a precursor ion mass tolerance of 5 ppm. Excellent detection limits, reproducibility, linearity and accuracies were obtained. For instance, for pyraclostrobin, thiophanate-methyl and tebuconazale LOQs were determined to be 0.5 ppb, 1 ppb and 0.5 ppb, respectively. CV values at LOQ were 1.9 % for pyraclostrobin and thiophanate-methyl and 2.6 % for tebuconazale. The calculated amounts at LOQ were within 11%, 9% and 13% of the spiked amount for pyraclostrobin, thiophanate-methyl and tebuconazole, respectively. These pesticides have been reported by FDA1 to be present in human foods at high frequencies and they are monitored by FDA. Overall, for 246 pesticides, out of the 250 tested, the LODs were at/or below 5 ppb with 226 pesticides having LODs at/or below 1 ppb. LOQs were below 5 ppb for 243 pesticides tested. When the AcquireX workflow was applied for automated background exclusion we observed a significant increase in the number of library matches compared to DDA, especially at the lower concentration levels. For instance, at a spiked concentration of 0.5ppb the presence of 20 pesticides was confirmed via library search with DDA. When utilizing the AcquireX workflow, at the same concentration level, the presence of 142 pesticides was confirmed. Similar trends were observed at a concentration level of 1 ppb in which we observed 173 library matches with AcquireX versus 72 library matches with DDA.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-05

Coauthors
Dipankar Ghosh, Thermo Fisher Scientific
Anastasia Kalli, Thermo Fisher Scientific
Seema Sharma, Thermo Fisher Scientific

Trace concentration determination of phthalates in non-PVC food packaging

Katherine Carlos, Lowri de Jager, and Timothy Begley

Corresponding Author
Katherine Carlos, katherine.carlos@fda.hhs.gov
FDA CFSAN

Abstract
PVC is a common food contact material that can be plasticized to increase its flexibility. Phthalates are one of many chemical compounds that are used as plasticizers in PVC. Transfer of plasticizers from packaging to the surfaces of foods or other materials can occur. In recent years, there has been renewed interest in understanding the potential health effects of phthalates, as well as the possible human exposure levels. However, there is limited information available about the major routes of exposure to phthalates. The concentrations that can be expected in most food products and non-plasticized food contact materials are several orders of magnitude lower than the concentrations that can be found in plasticized PVC. The significantly different concentrations require different methodology for their extraction and detection. Due to the widespread use of plasticized PVC in many commercial applications, background concentrations of phthalates are a concern when doing laboratory analyses. A liquid-liquid extraction with dichloromethane and hexane was used to extract phthalates from packaging. The extracts were then analyzed using a GC-MS/MS. Accuracy data showed spiked recoveries ranging from 71-124% in representative packaging. Phthalate concentrations in several different non-PVC printed and unprinted packaging will be presented This data will help provide the Agency important information on potential phthalate exposure to consumers via food consumption.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-06

Coauthors
Lowri de Jager, FDA CFSAN
Timothy Begley, FDA CFSAN

Non-Targeted Investigation of Extracted and Leached Chemicals from Packaging Materials by GC-MS and HR GC-MS

Brad Barrett, Elizabeth Humston-Fulmer, and Joe Binkley

Corresponding Author
Brad Barrett, Brad_Barrett@leco.com
LECO Corporation

Abstract
Migration of chemicals from packaging material into food products of serious concern. Packaging materials have the potential to contaminate food and beverages via extraction or leaching, which can impact the quality of the product, the integrity of the material, and cause health and safety concerns. Screening of contact materials is necessary to know what analytes are present and have the potential to migrate. Non-targeted analytical techniques are ideal when the analytes of interest are not known ahead of acquisition. GC-MS is a powerful tool for identifying unknowns in conjunction with high resolution GC-MS to assist with identification by accurate mass information. A novel benchtop GC-TOFMS system was used to investigate analytes that could be extracted from packaging materials.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-07

Coauthors
Elizabeth Humston-Fulmer, LECO Corporation
Joe Binkley, LECO Corporation

Direct Mass Spectrometric Identification of E-Waste in Polymeric Food Contact Materials

Luke K. Ackerman and Franky Puype

Corresponding Author
Luke K. Ackerman, luke.ackerman@fda.hhs.gov
US-FDA Center for Food Safety & Applied Nutrition

Abstract
Recycling of polymers can reduce waste and energy and protect water and land. Municipal waste streams struggle to maintain recycled polymer purity due to co-mingling & multi-polymer articles. Manufacture, deconstruction, and retail/captive venues can supply higher purity recycled polymer. However, it is difficult to source all recycled polymer demand from these niche streams. Contract manufacture and spot purchases of recycled polymers risk unknown contaminants being incorporated into the final products. One example has been brominated flame retardants (BFR) and waste electronic and electronic equipment (WEEE) components in reusable food contact articles (FCA) in Europe. BFRs and WEEE components are not approved for food contact materials. Methods to detect WEEE contaminants have used X-ray Florescence (XRF) of bromine, extraction GC-MS of BFRs, ICP-MS of rare-earth elements, and pyrolysis GC-MS for polymer degradants. If a rapid screening could be more specific for BFRs, inorganics or polymer mixes, then WEEE contaminated polymers could be identified and re-purposed sooner, recycled polymer more easily and routinely tested, and contaminated food contact materials (FCM) could be identified. Direct Analysis in Real Time, a thermal desorption and chemical ionization source for mass spectrometry, (DART-MS) was used to evaluate over a dozen polymer samples (including FCAs) with known concentrations of various BFRs, polymers, and WEEE components. Similarly, pure resins, BFR-free formulations, and pure WEEE component standards were analyzed. The DART-MS spectra of BFR and WEEE compounds, their transformations in polymers, and their ion chemistry were evaluated to identify the best ions for their detection, identification, and screening in various polymers and FCAs. WEEE components (including Antimony) were identified in WEEE contaminated polymers by DART-MS, and all BFRs in the samples were independently identified in the same samples by DART-MS.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-08

Coauthors
Franky Puype, ITC-Zlin

Determination of Free Bisphenol A in Commercially Packaged Ready to Consume Carbonated/Non-carbonated and Non-alcoholic Beverages with Immunoaffinity Column Purification and UPLC Fluorescence Detector

Jianmin Liu, Danrey Toth, Justine Yu, and Lingyun Chen

Corresponding Author
Jianmin Liu, Jianmin_liu@waters.com
Waters Corp

Abstract
A method for determination of bisphenol A (BPA) in carbonated, non-carbonated drinks, and non-alcoholic drinks was developed. The sensitivity, accuracy, and repeatability characteristics were evaluated. Replicates of a carbonated soft drink, orange juice with pulp and a dairy based coffee drink at spiking levels ranging from 0 to 32 ng/mL were analyzed on 1 to 3 separate days. Prepared samples were run through an immunoaffinity column containing antibodies specific for BPA. After the column was washed with water, BPA was eluted from the IAC with 80% methanol, and the eluate was directly injected into UPLC with FLD or concentrated and then injected into UPLC with FLD for separation, detection and quantitation depending on sample matrix. Results showed that LOD ranged from 0.06 to 0.08 ng/mL and LOQ ranged from 0.10 to 0.14 ng/mL, which were determined by using the least contaminated blank samples. Recoveries of BPA from all sample types at spiked levels ranged 1 to 16 ng/mL were between 93 and 100%; relative standard deviation (% RSDr) ranged from 0.71 to 8.38% depending on matrix and spiking levels. The BPA affinity column provides a new and reliable clean-up method for analyzing BPA in various complex sample matrix with high sensitivity and recoveries.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-09

Coauthors
Danrey Toth
Justine Yu
Lingyun Chen

DETERMINATION OF MULTI-MYCOTOXINS IN ASTRAGALUS ROOT BY IMUNOAFFINITY PURIFICATION AND LC-MS/MS

Jianmin Liu, Elise Palmer, Dan Mao, and Lingyun Chen

Corresponding Author
Jianmin Liu, Jianmin_liu@waters.com
Waters Corp

Abstract
The expanding use of herbal medicine, and in particular Traditional Chinese Medicine (TCM), leads to an increased need for effective quality control mechanisms to monitor for mycotoxin contamination during the growth, harvest and storage of cultivated plants. The World Health Organisation (WHO) defines herbal medicines as "naturally occurring, plant-derived substances with minimal or no industrial processing that have been used to treat illness within local or regional healing practices." Worldwide, the herbal medicine market is expected to reach $130 billion (USD) by 2023, with 70-80% of the global population relying on some form of such treatment. Mycotoxins are found in numerous cultivated herbal plants, and official regulations implemented. Here, we describe a novel LC-MS/MS method for the determination of multiple mycotoxins (total 13 types) in Astragalus root (common name: bei qi, huang qi, ogi, hwanggi, or milk vetch; latin name: Astragalus membranaceus). Sample was extracted with 70% methanol, and diluted with PBS and run through Myco6in1+ affinity column. Results showed that the LOD ranged from 0.1 to 5ppb for 13 types of mycotoxins tested, with about 73 to 102% recoveries within the tested linear ranges.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-10

Coauthors
Elise Palmer
Dan Mao
Lingyun Chen

Application of an Automated Sample Preparation System for Mycotoxin Analysis in Foods

Kai Zhang

Corresponding Author
Kai Zhang, kai.zhang@fda.hhs.gov
FDA/CFSAN

Abstract
Interest in replacing manual operations using robotic tools justifies the need of automation systems that can handle repetitive and high-volume tasks. In the field of food analysis, automated sample preparation is still in its early stage, though such practices have been commonly used in areas of drug screening and routine clinic sample analysis. For food analysis, samples need to be processed prior to instrumental measurements through multiple steps such as homogenization, weighing, solid-phase extraction (SPE), solvent exchange, shaking, heating/cooling, evaporation, filtration, centrifugation, and derivatization. This makes automated sample preparation a challenge as each step requires different tools, labware, and sample vessels. A highly automated sample preparation workflow requires integration of required devices and capability of transportation and storage so that samples can be processed and moved through each sub-step. In this proof of concept study, an automation system, Chemspeed Swing XL® was evaluated, focusing on sample preparation for the determination of mycotoxins using liquid chromatography–mass spectrometry (LC-MS). The system is equipped with two robotic arms, various modular tools and storage racks, and can conduct transport, gravimetric and volumetric dispensing, shaking, capping/decapping, filtration, and centrifugation without human assistance. Fortified corn, peanut butter, milk, and certified reference materials were used to evaluate the performance of the system. Our results suggest that automation is a promising alternative to manual operation and has potential for application to food analysis. Furthermore, automation may assist laboratories achieve a high degree of standardization for routine mycotoxin analysis.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-11

Preparation and characterization of an aflatoxin B1 calibration solution in the framework of a capacity building program for mycotoxin metrology

Gustavo Martos, Steven Westwood, Lucía Casas, Laura Vanessa Morales, Rachel Torkhani, Magali Bedu, Xiang Jiang Li, Ralf Josephs, and Robert Wielgosz

Corresponding Author
Gustavo Martos, gustavo.martos@bipm.org
Bureau International des Poids et Mesures (BIPM)

Abstract
Climatic conditions, pest control and poor harvest and storage practices are associated with the natural occurrence of mycotoxin contaminants in food and agricultural products worldwide. Among the most prevalent and toxic are aflatoxins, fumonisins, ochratoxin A, zearalenone, deoxynivalenol and patulin. These fungal metabolites threaten human and animal health and represent a major concern for international trading and legislation enforcement. The development of an adequate metrology infrastructure is a key priority in highly impacted countries to underpin mycotoxin analysis, and this is being supported by a Capacity Building and Knowledge Transfer (CBKT) program for Metrology for Safe Food and Feed started in 2016 and coordinated by the BIPM. Nineteen visiting scientists from national metrology institutes (NMIs) seeking to develop capabilities in this area have taken part in this project, with a special focus in the production and value assignment of mycotoxin calibrants. A first comparison on Zearalenone calibration solutions, CCQM-K154a, has recently been completed, supporting the mycotoxin calibrant production and characterization capabilities in nine NMIs. In the present poster, a new CBKT project that started in 2019 on aflatoxin B1 (AfB1) is presented. It consists in the preparation of a pure AfB1 calibration solution, the characterisation of the homogeneity and stability of the batch, including the main impurities, and the value assignment by gravimetric and analytical methods. The source material was assigned for its mass fraction content (purity) by quantitative nuclear magnetic resonance and liquid chromatography – tandem mass spectrometry (LC-MS2). The analytical measurements of the calibration solution were performed by LC-UV for the main component and LC-MS2 for related structure impurities. A key comparison is planned for 2020 and will demonstrate the equivalence of NMI capabilities to produce AFB1 calibration solutions.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-12

Coauthors
Steven Westwood, Bureau International des Poids et Mesures (BIPM)
Lucía Casas, Laboratorio Tecnológico del Uruguay (LATU)
Laura Vanessa Morales, Instituto Nacional de Metrología de Colombia (INM)
Rachel Torkhani, Institut National de Recherche et d'Analyse Physico-Chimique (INRAP)
Magali Bedu, Bureau International des Poids et Mesures (BIPM)
Xiang Jiang Li, National Institute of Metrology (NIM), China
Ralf Josephs, Bureau International des Poids et Mesures (BIPM)
Robert Wielgosz, Bureau International des Poids et Mesures (BIPM)

The Impact of Polarity Switching in LC-MS/MS for Analyzing Large Panels of Mycotoxins and Metabolites in Agricultural Samples

Oscar G. Cabrices, Jianru Stahl-Zheng, and Daniel McMillan

Corresponding Author
Oscar G. Cabrices, oscar.cabrices@sciex.com
SCIEX

Abstract
Mycotoxins are toxic fungal metabolites, which are derived from certain molds and fungi. The most important classes of mycotoxins including the highly carcinogenic Aflatoxins (e.g. AFB1), trichothecenes (e.g. DON), Fumonisins (e.g. FB1), Ochratoxins (OTA) and Zearalenone (ZEN) and several others are regulated in many countries. On the other hand, a living plant can change the chemical structure of these toxins producing so-called “masked mycotoxins”, which are often are undetectable by traditional testing methodologies like immunoassay ELISA kits and HPLC coupled to fluorescence detection.

This research study involved the use of a Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS) targeting a large suite of 530 mycotoxins, masked mycotoxins and their metabolites in different agricultural commodities. Sample preparation involved solvent extraction with Acetonitrile/Water/Acetic followed by a 1:1 dilution with LC mobile phase. Chromatographic separation was performed using a Polar C18 Column (2.6µm, 100 x 2.1mm) over a run time of 22 minutes using an acquisition method of 1040 Multiple Reaction Monitoring (MRM) MS/MS transitions.

Trace detection of all analytes at low part-per-billion concentration levels in matrix was studied by testing different Positive/Negative electrospray ionization polarity switching settling times (5ms, and 50 ms) experiments. The minimum number of data points required and Retention Time (RT) acquired across key positive compounds were determined, to meet ion ratio acceptance criteria. Furthermore, method linearity, sensitivity, data points, reproducibility, carryover, and robustness were evaluated using SANTE/11813/2017 guidelines. Incurred corn and barley samples were tested with this methodology, where “masked mycotoxins” (e.g., aspinonene) were detected and confirmed through the ion ratios of their quantitative and confirmatory MRM transitions.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-13

Coauthors
Jianru Stahl-Zheng, SCIEX
Daniel McMillan, SCIEX

A Year-to-Year Comparison of the Occurrence of 3-Monochloro-1,2-Propanediol (3-MCPD) Esters and Glycidyl Esters in Infant Formulas Purchased in the U.S. and Germany

Jessica Beekman, Linda Kanz, Michael Granvogl, and Shaun MacMahon

Corresponding Author
Jessica Beekman, jessica.beekman@fda.hhs.gov
U.S. Food and Drug Administration

Abstract
Fatty acid esters of 3-monochloro-1,2-propanediol (3-MCPD), 2-monochloro-1,3-propanediol (2-MCPD), and glycidol are process-induced chemical contaminants found in refined edible oils. Formed during the deodorization step of the refining process, these compounds are considered potentially carcinogenic and/or genotoxic, making their presence in refined oils and foods a source of potential concern. Dietary exposures to bound 3-MCPD and glycidol from consumption of infant formulas are of particular interest because formulas are the sole or primary food source for some infants. Over the last several years, research efforts at the U.S. Food and Drug Administration (FDA) have focused on the analysis of these contaminants in infant formulas in an effort to estimate levels of exposure. This presentation will briefly discuss the extraction and detection protocol (liquid chromatography-tandem mass spectrometry (LC-MS/MS)) employed in our laboratory, as well as the results of several occurrence studies encompassing over 400 infant formula products (from the U.S. and Germany) purchased between 2013 and 2019. The data show a wide range of 3-MCPD and glycidyl ester concentrations across a variety of infant formulas, as well as a decrease in contaminant concentrations from 2013 to 2018 among some infant formula manufacturers.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-14

Coauthors
Linda Kanz, University of Hohenheim
Michael Granvogl, University of Hohenheim
Shaun MacMahon, U.S. Food and Drug Administration

Examination of Heavy Metal Contamination found in Raisins, Sultanas & Currants by ICP-MS

Patricia Atkins, Robert Lockerman, Tina Restivo, and Carlye McConnell

Corresponding Author
Patricia Atkins, patkins@spex.com
SPEX CertiPrep

Abstract
Over the last few years, studies have found high levels of contamination in grapes and grape products such as juice and wine. Recent studies have been conducted showing the presence of arsenic in apple juices and wine. Arsenic based pesticides, particularly lead arsenate, were in widespread use around the world up until the late 1980's and 90s. Despite arsenic residue being recognized as a potential problem from the turn of the century, lead arsenate was one of the most widely used pesticides in the nation and was applied to millions of acres of crops through the 1940's. Lead arsenate was the most commonly applied pesticide in fruit orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, samples were obtained of popular organic and regular raisins, sultanas and currants from various stores in the US, UK and Germany. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-15

Coauthors
Robert Lockerman, CEM Corporation
Tina Restivo, CEM Corporation
Carlye McConnell, SPEX CertiPrep

Examination of Elemental Composition & Toxic Metals in Bread Spreads

Patricia Atkins, Robert Lockerman, Tina Restivo, and Carlye McConnell

Corresponding Author
Patricia Atkins, patkins@spex.com
SPEX CertiPrep

Abstract
Many popular breakfast and bread spreads are natural products composed of fruit, nuts, seeds and yeasts. Children are frequent consumers of many of these popular spreads. Studies of individual spread components such as grapes, nuts and cocoa beans have reported significant amounts of heavy metal contamination. Lead arsenate was the most commonly applied pesticide in fruit & nut orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned. In this study, various samples of bread spreads including fruit spreads, peanut butter, nut butters, yeast spreads and cocoa spreads were tested for heavy metal contamination. Samples were digested using microwave digestion and testing by ICP-MS to determine heavy metal contamination possible in these common foods.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-16

Coauthors
Robert Lockerman, CEM Corporation
Tina Restivo, CEM Corporation
Carlye McConnell, SPEX CertiPrep

Arsenic species in edible seaweeds commercialized in the United States

Mesay Mulugeta Wolle, Sara Handy, Todor Todorov and Sean D. Conklin

Corresponding Author
Sean D. Conklin, sean.conklin@fda.hhs.gov
Food and Drug Administration, Center for Food Safety and Applied Nutrition

Abstract
Seaweeds are increasingly being cultivated for food as they are rich in nutrients, such as amino acids, Vitamin K, and iodine. On the other hand, seaweeds are known to accumulate arsenic in dozens of chemical forms, some of which are of known toxicities and others have yet to be fully elucidated for any potential effects. Most risk assessment practices associated with dietary arsenic are based on monitoring inorganic arsenic, which is a Class I carcinogen. Such an approach is generally adequate, as most products are known to accumulate arsenic in forms of defined properties. However, the approach may leave species of potential or unknown toxicities unidentified when applied to seaweeds, where arsenic has a complex and variable distribution of species. Comprehensive speciation analysis which aims at capturing a complete picture of the distribution of arsenicals is recommended. The poster presents a wide-ranging speciation analysis of arsenic in edible seaweeds commercialized in the United States. Samples were purchased from local supermarkets and online and analyzed by methods recently developed [1] and single-lab validated [2] at the FDA. The accuracy of the analytical results was substantiated by analyzing certified reference materials and using spike recovery tests.

References
[1] M. M. Wolle, S. D. Conklin; Anal Bioanal Chem 410 (2018) 5675
[2] M. M. Wolle, S. D. Conklin; Anal Bioanal Chem 410 (2018) 5689

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-17

Coauthors
Mesay Mulugeta Wolle, Food and Drug Administration, Center for Food Safety and Applied Nutrition
Sara Handy, Food and Drug Administration, Center for Food Safety and Applied Nutrition
Todor Todorov, Food and Drug Administration, Center for Food Safety and Applied Nutrition

Non-Targeted and Suspect Screening using LC/HR-MS to Identify Unknowns: Quality Controls and Retention Time Prediction

Christine M. Fisher, Jacob H. Premo, and Ann M. Knolhoff

Corresponding Author
Christine M. Fisher, Christine.ODonnell@fda.hhs.gov
Food and Drug Administration, Center for Food Safety and Applied Nutrition

Abstract
While it is critical to monitor hazardous compounds or classes of compounds for food samples using targeted screening, these analytical methods will not detect other potentially harmful compounds that may be present. Thus, the development of non-targeted and suspect screening methods is necessary for ensuring public health. Liquid chromatography coupled to high-resolution mass spectrometry (LC/HR-MS) is one analytical technique that can be used for non-targeted screening because thousands of compounds from broad molecular classes can be detected in a single analysis. Furthermore, molecular formulae can be generated for detected compounds of interest. However, these information-rich data sets can be challenging to analyze, especially given the diversity of food samples and their inherent chemical complexity, with components that are present in a wide range of concentrations. Because data processing/analysis is the most time-intensive step for these workflows, much of our effort has focused on the development, optimization, and testing of these strategies. Adequate QC standard mixtures are necessary to test the performance of each processing step, so we have developed a mixture that can be used for this purpose and the various applications will be discussed. Considerations included achieving diversity of compounds in terms of ionizability, elemental composition, molecular weight¸ and retention time. This standard mixture was also utilized to predict retention time to reduce the number of false positives found with suspect and non-targeted screening approaches. Retention time prediction was initially tested using a large mixture of pesticides (Restek pesticide mix), where 82% of the compounds were predicted within +/- 4.5 min using a 30 min gradient. We are further testing the model with other compound classes and will discuss thresholds that can be used for unknown identification and the extent to which this strategy will reduce false positives.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-18

Coauthors
Jacob H. Premo, Food and Drug Administration, Center for Food Safety and Applied Nutrition
Ann M. Knolhoff, Food and Drug Administration, Center for Food Safety and Applied Nutrition

Miniature Mass Spectrometers for Field Detection of Food Chemical Contaminants and Residues

Christina Ferreira, Zhuoer Xie, and R. Graham Cooks

Corresponding Author
Christina Ferreira, cferrei@purdue.edu
Department of Chemistry and Bindley Bioscience Center, Purdue University

Abstract
Our group has been developing ion trap–based miniature mass spectrometer (Mini MS) systems for many years and demonstrated their applicability to pesticide and chemical contaminants detection, therapeutic drug monitoring, illicit drug detection, and preclinical pharmacokinetic. The miniature MS are stand-alone systems without external pumps or gas suitable to field analysis and into law enforcement or Federal quality control settings for diverse purposes such as pesticide traces and adulteration determination. The important requirements for a Mini MS are to display enough mass resolution to separate analyte ions from other components, as well as appropriated sensitivity and selectivity for the intended measurement. The instruments are also tunable to a specific application (e.g., pesticide determination, explosives or narcotics detection, reaction monitoring, etc.). To be portable, we developed rugged, inexpensive electronics, and minimized power consumption, enabling operation from battery power. To take advantage of portability, the Mini MS instruments have ambient ionization sources for screening samples without purification, on-site, regardless of composition, phase, or complexity. Recently, we launched a workflow for rapid analysis of various types of cosmetic and foodstuff samples using paper spray ionization, extraction spray ionization and slug-flow microextraction for direct analysis of Sudan Reds, parabens, antibiotics, steroids, bisphenol and plasticizer from raw samples with complex matrices. Limits of detection as low as 5 μg/kg were obtained for target analytes. On-line derivatization was also carried out for analysis of steroid in cosmetics. Another newly breakthrough was implementing precursor ion and neutral loss scanning capabilities on a Mini 12 miniature rectilinear ion trap mass spectrometer, which displayed better mass resolution and limit of detection compared to a commercial Thermo linear trap quadropole (LTQ) linear ion trap.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-19

Coauthors
Zhuoer Xie, Department of Chemistry, Purdue University
R. Graham Cooks, Department of Chemistry, Purdue University

Certification of Marine Toxins by Quantitative NMR (qNMR) and Isotope Dilution MS (IDMS)

Markus Obkircher, Alexander Rueck, Christine Hellriegel, Rudolf Koehling, and Matthias Nold

Corresponding Author
Matthias Nold, matthias.nold@merckgroup.com
MilliporeSigma

Abstract
Since the presence of marine toxins in shell fish and sea food is an emerging worldwide problem, fast and sensitive LC-MS methods were established for food safety testing.[1] Therefore, the access to well characterized reference materials for a precise and accurate quantitation of these different toxins has become an increased need in the market. These reference materials should be characterized and prepared according to ISO/IEC 17025 and ISO 17034. In order to achieve certification of such small batches according to this double accreditation at the highest metrological level, a combined setup of quantitative NMR (qNMR)[2],[3] and Isotope Dilution MS (IDMS)[4],[5] was successfully established.[6] In a first step, the accurate concentration of a dissolved toxin is determined by a series of 1H-qNMR measurements. Gravimetric dilution and ampule filling deliver the final product with a certified concentration and an associated expanded uncertainty, which can be subsequently applied in an HPLC-IDMS experiment that results in a concentration for the stable isotope labeled analog. Gravimetric IDMS experiments are also carried out to determine the homogeneity and stability contribution to the overall uncertainty. These concepts were successfully adopted for the certification of multiple toxins despite their partial instability and tendency to undergo rearrangement reactions. Several paralytic shellfish toxins (PST) were developed, for example the well-known Neosaxitoxin or Saxitoxin and their stabile isotope labeled analogs 15N7-Neosaxitoxin and 15N7-Saxitoxin. In addition, other toxins like Okadaic acid, PTX11, GTX-6, Gymnodimine, Pinnatoxin E, F and F as well as several Brevetoxins could be made available to testing laboratories.

References

[1] M. J. Boundy et al, Journal of Chromatography A, 1387, 1-12, 2015.
[2] M. Weber, Ch. Hellriegel, A. Rueck, R. Sauermoser, J. Wuethrich, Accreditation and Quality Assurance, 18(2), 91- 98, 2013.
[3] M. Weber, Ch. Hellriegel, A. Rueck, J. Wuethrich, P. Jenks, Journal of Pharmaceutical and Biomedical Analysis, 93, 102-110, 2014.
[4] A. Breidbach, ThOS36-02, IMSC 2104, Geneva, CH.
[5] M. Sargent, Guidelines for Achieving High Accuracy in IDMS, RSC (LGC), Cambridge 2002.
[6] R. Koehling, E. Allenspach, Ch. Hellriegel, A. Rueck, J. Boertz, F. Wahl, M. Weber, M. Obkircher, Poster DGMS, 2016

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-20

Coauthors
Markus Obkircher, MilliporeSigma
Alexander Rueck, MilliporeSigma
Christine Hellriegel, MilliporeSigma
Rudolf Koehling, MilliporeSigma

Perfluoroalkyl Substance (PFAS) Analysis in Drinking Water, Sediments and Food Samples by QuEChERS, SPE, and LC-MS/MS

Scott Krepich, Nick Mitchell

Corresponding Author
Scott Krepich, ScottK@phenomenex.com
Phenomenex

Abstract
Perfluoroalkyl substances (PFAS) are a class of highly stable synthetic organic compounds used in a wide variety of industrial and commercial applications including surface treatment for textiles, packaging materials, non-stick cookware, and firefighting foams. PFASs are characterized by a hydrophobic fully fluorinated alkyl chain and a hydrophilic functional group. They are persistent in the environment due to the exceptional stability of the C-F bond. These have been detected throughout the global environment, food products, even human plasma. PFASs are associated with various adverse health effects, they are bioaccumulative, ubiquitous, and their analysis level requirements are very low, to account for an expected lifetime of exposure. There are several methods available for the extraction and analysis of PFAS in aqueous samples. However, very few procedures are available for extracting these compounds in solid matrices such as sediments and food samples. Presented are three methods making use of various sample preparation techniques for the analysis of PFAS. The methods include, direct inject technique for drinking water, QuEChERS for sediment samples, and QuEChERS followed by SPE for food samples (milk, eggs, and fish tissue). All are validated procedures and makes use of LC-MS/MS.

Poster Category: Chemical Contaminants and Residues
Poster Number: CHCR-21

Coauthors
Nick Mitchell, Phenomenex