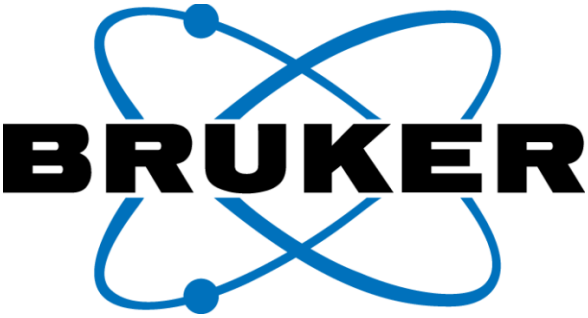
November 3, 2015 (12:30–13:30)



VENDOR SEMINAR:

Elemental and Mass Spectrometric Solutions for the Analysis of Toxicants

Introduction to Bruker Daltonics solutions for food safety testing

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Analysis of α-amanitin, β-amanitin and muscarine mushroom toxins in urine by UHPLC-QTOF mass spectrometry

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For centuries, mushrooms have been a popular and often indispensible ingredient in the most exquisite cuisines around world. Their taste is unique, their caloric value is low and they are full of vitamins and minerals. Here, in the Czech Republic mushrooms grow everywhere and consequently mushroom picking is very popular and widespread, so much so that there is a common belief that mushrooming is a Czech 'national sport.' However, some varieties of mushroom contain lethal toxins and the most common cause of mushroom poisoning occurs through inadvertent misidentification of the varieties picked. Mushroom poisoning through dietary error resulting in hospitalization after ingestion is occasionally confirmed, and in 2014 out of 28 cases two were found to be positive.

Muscarine is the principal toxin in fungi of the genus Inocybe, Clitocybe and together with isoxazole derivatives ibotenic acid and muscimol is also present in the genus Amanita (*Amanita pantherina, Amanita muscaria* and others). *Amanita pantherina* is often confused with *Amanita spissa or Amanita rubescens* and *Amanita muscaria* is abused for its hallucinogenic effects.

The *Amanita phalloides* poisoning is rare, but may cause severe or even fatal intoxication. Amanita mushrooms contain amatoxins such as α-amanitin and β-amanitin and phallotoxins such as phallacidin. *Amanita phalloides* is often confused with agaricus or russula aeruginea.

Muscarine was used as a diagnostic marker for poisonings of *Amanita pantherina* and *Amanita muscaria*. α-amanitin and β-amanitin were used as diagnostic markers for *Amanita phalloides* poisoning. Phallacidin was chosen as an internal standard (IS) because it is not absorbed from the intestine.

Aims:

The aim of the present study was to develop a fast and sensitive method for simultaneous analysis of α-amanitin, β-amanitin and muscarine in human urine by solid-phase extraction (SPE) and ultra-high-performance liquid chromatography coupled with ultra-high-resolution TOF mass spectrometry.

Screening dioxin and pesticide residues in food extracts using GC-APCI coupled to high-resolution QTOF Mass Spectrometry

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The use of accurate mass QTOF-LC/MS with electrospray ionization for target pesticide screening enables the identification of hundreds of pesticides in a single run. On the other hand, GC/MS is well suited to these compounds and generally exhibits less matrix effects whilst producing lower chemical background. GC/MS is also well suited for trace analysis of other compound classes like polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polybrominated diphenyl ethers (PBDE). As they belong to the class of persistent organic pollutants (POPs) they are one of the major concerns in present environmental discussion. Due to the accumulation in the food chain it is of general interest to analyze them with good sensitivity and confidence.

For pesticide analysis a standard mix consisting of 60 representative pesticides was spiked into fruit and vegetable matrices selected according to their relevance in food analysis and and their varied physiochemical characteristics, such as molecular mass, chemical composition, polarity and volatility. The mix contained amongst others: azinphos-Methyl, chlorpropham, diazinon, dimethoate, EPN, imazalil, myclobutanil and pirimicarb. 1 µl of each sample was injected and separated using a Restek Rxi-5ms capillary (30m, 0.25 mm ID, 0.25 µm film). The GC column was interfaced to a Q-TOF-MS (Impact II, Bruker Daltonik GmbH) with a GC-APCI source operated in both positive and negative ionization modes. Data were acquired from 50-1000 m/z at minimum of 4 Hz. All files were acquired with automatic mass calibration at the beginning of each GC/MS run with a perfluorinated calibration standard. All data were processed with the TASQ 1.0 software (Bruker Daltonik GmbH). The GC-APCI-Q-TOF-MS system was calibrated for quantification with the 60 pesticide standard in the concentration range of 0.05 to 500 pg/µl. Limits of quantification (LOQ) for most of the pesticides were found to be in the range well below 10 pg/µl with RSDs between 5 and 10 % (N=3).

As key substances for POPs we analyzed decabromodiphenyl ether (DecaBDE) and 2,3,7,8-tetrachlordibenzodioxin (2,3,7,8-T4CDD) with the GC-APCI-Q-TOF-MS setup. PBDEs are among the EU priority substances. DecaBDE is the most difficult PBDE to analyze, because it is less volatile and additionally thermolabile. DecaBDE showed a good response at a concentration of 1 pg on column, LOD was even lower. The analytical working range was between 1-40 pg on column.

2,3,7,8-T4CDD is the most toxic substance of the PCDD/PCDF compounds. 2,3,7,8-T4CDD was detected as [M]+ signal and the LOD of 2,3,7,8-T4CDD was <0.1 pg on column. The calibration curve showed an analytical working range between 0.1-2000 pg on column. Using GC-APCI coupled to high resolution QTOF-MS we achieved excellent detection limits at the relevant environmental maximum residue limit levels.

A rapid and cost-efficient method for the measurement of Arsenic in rice

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Almost half of the world's population eats rice every day, in many cases several times per day. Therefore, it is considered that rice is the dominant source of inorganic arsenic in the human diet. Rice contains significant amounts of inorganic arsenic with concentrations often between 0.1 to 0.4 mg arsenic/kg dry mass or higher.

Although it is known that chronic arsenic exposure is linked with cancers of the bladder, lungs, skin and prostate, as well as heart disease, only a few countries have established maximum levels (MLs) for total arsenic in food. In 2011 the World Health Organisation (WHO) has published a recommendation showing a maximum level of 200 µg/kg of inorganic As in polished rice.

The accurate detection if low levels of As in food by common atomic spectroscopy methods requires a dedicated laboratory infrastructure with sample preparation equipment (microwave digestion), cooling water and gas supplies. In contrast to that Total Reflection X-Ray Fluorescence (TXRF) spectrometry is an easy-to-use method which requires minimum sample preparation and no gases or any other media for an accurate multi-elements analysis in the ppb-range.

This paper describes the successful application and method development for the measurement of As in rice by TXRF. The new S2 PICOFOX Ultra Efficiency with a 50W micro focus tube and a 60 mm² XFlash silicon drift detector offers detection limits below 50 µg/kg after a rapid sample preparation without any digestion.