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Pesticides, Contaminants, and Impurities

Accurate Mass Fragment Library for Rapid Analysis of Pesticides on Produce Using Ambient Pressure Desorption Ionization with High-Resolution Mass Spectrometry

Kern, S., Lin, L., & Fricke, F. (2014). Journal of The American Society for Mass Spectrometry, 25(8), 1482–1488. doi:10.1007/s13361-014-0912-1

U.S. food imports have been increasing steadily for decades, intensifying the need for a rapid and sensitive screening technique. A method has been developed that uses foam disks to sample the surface of incoming produce. This work provides complimentary information to the extensive amount of published pesticide fragmentation data collected using LCMS systems (Sack et al. Journal of Agricultural and Food Chemistry, 59, 6383-6411, 2011; Mol et al. Analytical and Bioanalytical Chemistry, 403, 2891-2908, 2012). The disks are directly analyzed using transmission-mode direct analysis in real time (DART) ambient pressure desorption ionization coupled to a high resolution accurate mass-mass spectrometer (HRAM-MS). In order to provide more certainty in the identification of the pesticides detected, a library of accurate mass fragments and isotopes of the protonated parent molecular ion (the [M+H]+) has been developed. The HRAM-MS is equipped with a quadrupole mass filter, providing the capability of "data-dependent" fragmentation, as opposed to "all -ion" fragmentation (where all of the ions enter a collision chamber and are fragmented at once). A temperature gradient for the DART helium stream and multiple collision energies were employed to detect and fragment 164 pesticides of varying chemical classes, sizes, and polarities. The accurate mass information of precursor ([M+H]+ ion) and fragment ions is essential in correctly identifying chemical contaminants on the surface of imported produce. Additionally, the inclusion of isotopes of the [M+H]+ in the database adds another metric to the confirmation process. The fragmentation data were collected using a Q-Exactive mass spectrometer and were added to a database used to process data collected with an Exactive mass spectrometer, an instrument that is more readily available for this screening application. The commodities investigated range from smooth-skinned produce such as apples to rougher surfaces like broccoli. The minimal sample preparation and absence of chromatography has shortened the analysis time to about 15 min per sample, and the simplicity and robustness of the technique make it ideal for rapid screening.

Determination of the aflatoxin M1 (AFM1) from milk by direct analysis in real time – mass spectrometry (DART-MS)

Busman, M., Bobell, J. R., & Maragos, C. M. (2015). Food Control, 47(0), 592–598. doi:10.1016/j.foodcont.2014.08.003

Certain fungi that grow on crops can produce aflatoxins, which are highly carcinogenic. One of these, aflatoxin B1 can be metabolized by mammals to aflatoxin M1, a form that retains potent carcinogenicity and which can be excreted into milk. Direct analysis in real time (DART) ionization coupled to a high resolution mass spectrometer (MS) was used for the rapid quantitative analysis of a common form of aflatoxin, AFM1, extracted from cow milk. Sample preparation procedure and instrument parameter settings were optimized to obtain sensitive and accurate determination of AFM1. The lowest calibration level (LCL) for aflatoxin AFM1 was 0.1 µg/kg. Quantitative analysis was performed with the use of matrix-matched standards employing a 13C-labeled internal standard for AFM1. DART-MS of spiked milk extracts gave linear response over the range of 0.1-2.5 µg/kg. Good recoveries (94.7-109.2%) and repeatabilities (RSD 13.5-9.6%) were obtained at spiking levels of 0.5 and 2.0 µg/kg. The results of the study further demonstrate the potential of ambient ionization-MS techniques for the sensitive, convenient and rapid quantitative determination of mycotoxins from difficult matrices.

Non-visible print set-off of photoinitiators in food packaging: detection by ambient ionization mass spectrometry

Bentayeb, K., Ackerman, L. K., Lord, T., & Begley, T. H. (2013). Food Additives & Contaminants: Part A, 30(4), 750–759. doi:10.1080/19440049.2012.762694

Direct Analysis in Real Time coupled to Time of Flight Mass Spectrometry (DART/TOF-MS) was used to detect the non-visible set-off of photoinitiators on the food contact surface of three different packages. The samples were intentionally under-cured to provoke set-off. Twelve commercially available photoinitiators were included in the ink formulations including α -amino-, morpholino, and α hydroxy benzophenones, thioxanthones, arylphosphine oxide and three polymeric versions of these. Major colors of the packages' prints were analyzed, as well as the specific areas of the inner surface in contact with them. Larger quantities of photoinitiators were detected on the food contact areas in contact with the darker colors of the images. Speed-cure 7005 and 4phenylbenzophenone were the compounds most susceptible to set-off in each of the samples by DART response. An identification protocol for unknown set-off compounds was tested resulting in the set-off detection of diethylene glycol ethers, erucamide and acrylates, and confirmed by solvent extraction GC-MS analysis. Finally, DART/TOF-MS was scanned across transects of the food contact side of packages to map the presence of photoinitiators. Higher photoinitiator signals were observed in patterns corresponding to the printed image, suggesting DART/TOF-MS might image print set-off.

Direct Peel Monitoring of Xenobiotics in Fruit by Direct Analysis in Real-Time Coupled to a Linear Quadrupole Ion Trap-Orbitrap Mass Spectrometer

Farré, M., Pico, Y., & Barcelo, D. (2013). Analytical Chemistry, 85(5), 2638–2644. doi:10.1021/ac3026702

Study of xenobiotics present in fruits peel by exposing it (without any pre-treatment) to direct analysis in real time coupled to a high resolution orbitrap mass spectrometer (DART-HRMS) is reported for the first time. Variables as DART gas heater temperature and pressure, source-to-MS distance and sample velocity are investigated. The analysis of one sample by DART-MS lasts ca. 1 min, and the benefits of both high-resolution and tandem mass spectrometry to elucidate non-target or unknown compounds are combined. Identification of post-harvest fungicides, antioxidants and sugars in fruit peel is performed in the positive ion mode. Possible elemental formula is suggested for marker components. The lowest imazalil concentration that could be detected by this system is 1 ng (equivalent to a concentration of ca. 300 µg kg-1), which is wellbelow the maximum residue limit. For oranges and apples, direct peel exposition demonstrated good interday precision (within 20 % for any concentration) and proper linearity (R2≥0.99), with a dynamic range from 1 to 2500 ng for apple. A comparison of the results obtained using the direct peel screening DART-based method is made with those obtained by DART analysis of solvent extracts, as well as those obtained analyzing these extracts by Ultra High Performance Liquid Chromatography Orbitrap Mass Spectrometry (UHPLC-Orbitrap). The results are in good agreement. Thus, the proposed method proves to be guantitatively accurate with indisputable identification specificity. As an independent method, the approach of direct scanning of peel is of high interest and of potential future within food analysis to guarantee safety, guality and authenticity.

Determination of the aflatoxin AFB1 from corn by direct analysis in real time – mass spectrometry (DART-MS)

Busman, M., Liu, J., Zhong, H., Bobell, J. R., & Maragos, C. M. (2014). Food Additives & Contaminants: Part A, 31(5), 932–939. doi:10.1080/19440049.2014.900572

Abstract Direct analysis in real time (DART) ionization coupled to a high resolution mass spectrometer (MS) was used for screening of aflatoxins from a variety of surfaces and the rapid quantitative analysis of a common form of aflatoxin, AFB1, extracted from corn. Sample preparation procedure and instrument parameter settings were optimized to obtain sensitive and accurate determination of aflatoxin AFB1, 84:16 acetonitrile water extracts of corn were analyzed by DART-MS. The lowest calibration level (LCL) for aflatoxin AFB1 was 4 µg/kg. Quantitative analysis was performed with the use of matrix-matched standards employing the ¹³C-labeled internal standard for AFB1. DART-MS of spiked corn extracts gave linear response of the range 4-1000 µg/kg. Good recoveries (94-110%) and repeatabilities (RSD 0.7-6.9%) were obtained at spiking levels of 20 and 100 µg/kg with use of an isotope dilution technique. Trueness of data obtained for AFB1 in maize by DART-MS was demonstrated by analysis of corn certified reference materials.

Development of a rapid screening method to determine primary aromatic amines in kitchen utensils using direct analysis in real time mass spectrometry (DART-MS)

Paseiro-Cerrato, R., Noonan, G. O., & Begley, T. H. (2013). Food Additives & Contaminants: Part A, 31(3), 537–545. doi:10.1080/19440049.2013.867366

Primary aromatic amines (PAAs) are a group of substances with undesirable health effects, that are used in a variety of commercial products. Several recent studies, using a number of screening and confirmatory methods, have reported the migration of PAAs from some kitchen utensils into acetic acid 3% (w/v). Many of these methods require significant sample preparation, therefore the aim of this work was to determine if direct analysis in real time mass spectrometry (DART-MS) could be utilised as a rapid screening tool for the determination of PAAs in kitchen utensils. DART-MS results from direct analysis of the utensil have been compared with results of PAA migration by ultra high performance liquid chromatography tandem mass spectrometry (UPLC-MS/MS) method. The UPLC-MS/MS method had excellent linearity, appropriate sensitivity (LOD ≤ 1.5 μ g L⁻¹; LOQ \leq 4.5 μ g L⁻¹) repeatability from 2.4 to 13.2% and acceptable recoveries. DART-MS results were in good agreement with UPLC-MS/MS data, with 100% of non-compliant (PAA positive) samples successfully identified by DART-MS.

Direct analysis in real time high-resolution mass spectrometry for high-throughput analysis of antiparasitic veterinary drugs in feed and food

Martínez-Villalba, A., Vaclavik, L., Moyano, E., Galceran, M. T., & Hajslova, J. (2013). Rapid Communications in Mass Spectrometry, 27(3), 467– 475. doi:10.1002/rcm.6466

RATIONALE Direct analysis in real time (DART) is a novel ionization technique that has been demonstrated in numerous applications as a useful tool for fast and convenient mass spectrometry (MS)-based analysis of complex samples. In this study, the feasibility of DART ionization coupled to a high-resolution mass spectrometer utilizing an orbitrap mass analyzer (orbitrap MS) for highthroughput analysis of antiparasitic veterinary drugs was explored. METHODS To obtain the best DARTorbitrap MS performance, stepwise optimization of instrumental parameter settings, such as ionization gas temperature and mass resolving power, was performed. The optimized method was applied to feed and bovine milk samples previously extracted following a QuEChERS-like strategy. RESULTS Most antiparasitic drugs could be analyzed following the described method. Positive DART ionization provided the protonated molecules [M+H]+; in negative DART ion mode, deprotonated molecules [M–H]– were observed. As an exception, polyether ionophores could be observed as the sodiated adducts [M+Na]+. Samples of milk and feed were extracted using a modified QuEChERS method for the determination of benzimidazoles and coccidiostats respectively and quantification was carried out by matrix-matched calibration curves. CONCLUSIONS The combination of an analysis time of less than 1 min per sample and the possibility to acquire accurate masses under high mass resolving power (HR) makes the DART-HRMS technique an effective tool for rapid qualitative screening of antiparasitic veterinary drugs. Additionally, the results obtained in this study demonstrated the feasibility of this approach to quantify target analytes at levels down to 1 µg kg-1 for benzimidazolic compounds in milk and 0.25 mg kg-1 for coccidiostats in chicken feed.

Direct analysis in real time mass spectrometry for the rapid identification of four highly hazardous pesticides in agrochemicals

Wang, L., Zhao, P., Zhang, F., Li, Y., & Pan, C. (2012). Rapid Communications in Mass Spectrometry, 26(16), 1859–1867. doi:10.1002/rcm.6274

RATIONALE Direct analysis in real time (DART) is a new ion source technique, which is conducted in the open air under ambient conditions, applied to the rapid and direct analysis of any material (gases, liquids, and solids) with minimal or no sample preparation. In order to take advantage of the capacity of DART mass spectrometry for the realtime analysis of hazardous ingredients in commercial agrochemicals, a pilot study of rapid qualitative determination of hazardous pesticides was performed. METHODS Highly hazardous pesticides were identified by DART ionization coupled to a single-quadrupole mass spectrometer (DART-MS). Acetonitrile was chosen for dissolving samples prior to the analysis. Samples were analyzed by this technique in as little as 5 s. RESULTS Phorate, carbofuran, ethoprophos and fipronil were be detected directly from commercial agrochemicals. The ionization-related parameters (DART temperature, grid voltage and MS fragment) of these compounds were optimized to obtain highly response. Isotope patterns were taken into consideration for gualitative identification. Relative standard deviations (RSDs, n = 5) of 2.3–15.0% were obtained by measuring the relative abundance of selected isotopes. CONCLUSIONS This study showed that DART-MS technology was able to qualitatively determine the existence of highly hazardous pesticides in commercial pesticide formulations. It is suggested that this technology should be applied for routine monitoring in the market.

Rapid qualitative analysis of phthalates added to food and nutraceutical products by direct analysis in real time/orbitrap mass spectrometry

Self, R. L., & Wu, W.-H. (2012). Food Control, 25(1), 13–16. doi:10.1016/j.foodcont.2011.10.013

A recent food safety issue involves the contamination of a broad range of food and nutraceutical products from Taiwan with industrial plasticizers. Among the suspected contaminants are selected phthalic acid esters, such as benzyl butyl phthalate, dibutyl phthalate, diisobutyl phthalate, di-2-ethylhexyl phthalate, di-n-octyl phthalate, diisononyl phthalate, and diisodecyl phthalate. Described in this study is an analytical method to rapidly qualitatively analyze these compounds in a wide variety of food and nutraceutical matrices suspected in this crisis. The method utilizes direct analysis in real time (DART) ionization coupled to a Thermo Exactive orbitrap mass spectrometer. The method is shown to be capable of detecting these compounds at levels greater than 1.0 µg/mL in all food products examined and 0.5 µg/mL in most of the samples tested. In the nutraceutical samples tested, the compounds were detected at levels of 50 µg/g for all samples with some detected as low as 1.0 µg/g.

Novel approaches to analysis of 3chloropropane-1,2-diol esters in vegetable oils

Moravcova, E., Vaclavik, L., Lacina, O., Hrbek, V., Riddellova, K., & Hajslova, J. (2012). Analytical and Bioanalytical Chemistry, 402(9), 2871–2883. doi:10.1007/s00216-012-5732-1

A sensitive and accurate method utilizing ultra-high performance liquid chromatography (U-HPLC) coupled to high resolution mass spectrometry based on orbitrap technology (orbitrapMS) for the analysis of nine 3-chloropropane-1,2-diol (3-MCPD) diesters in vegetable oils was developed. To remove the interfering triacylglycerols that induce strong matrix effects, a clean-up step on silica gel column was used. The quantitative analysis was performed with the use of deuterium-labeled internal standards. The lowest calibration levels estimated for the respective analytes ranged from 2 to 5 µg kg -1. Good recovery values (89-120%) and repeatability (RSD 5-9%) was obtained at spiking levels of 2 and 10 mg kg -1. As an alternative, a novel ambient desorption ionization technique, direct analysis in real time (DART), hyphenated with orbitrapMS, was employed for no separation, high-throughput, semi-guantitative screening of 3-MCPD diesters in samples obtained by chromatographic fractionation. Additionally, the levels of 3-MCPD diesters measured in real-life vegetable oil samples (palm oil, sunflower oil, rapeseed oil) using both methods are reported. Relatively good agreement of the data generated by U-HPLC-orbitrapMS and DART-orbitrapMS were observed. With regard to a low ionization yield achieved for 3-MCPD monoesters, the methods presented in this paper were not yet applicable for the analysis of these contaminants at the naturally occurring levels.

Direct Analysis in Real Time (DART) Mass Spectrometry of Adulterants in Herbal Slimming Products using a Tandem Quadrupole MS and Data Directed Analysis

Jones, M., Twohig, M., Yu, K., Balogh, M., Tice, J., & Musselman, B. (2012). Planta Med, 78(05), P_127. doi:10.1055/s-0032-1307635

Several troubling studies show the adulteration of herbal slimming products with sibutramine is a common occurrence. Recent reports suggesting an increased risk of serious cardiovascular events (such as heart attack or stroke) in patients with known cardiovascular disease taking sibutramine have prompted the European Medicines Agency (EMA) to recommend that the use of sibutramine be suspended. The aim of this study is to develop specific methods for the rapid screening of herbal medicines for illicit adulteration with pharmaceutical drugs. Herbal slimming aids were purchased over the internet from store websites and auction sites. Samples were analysed using a direct analysis in real time (DART) interface and a tandem guadrupole mass spectrometer. Samples purchased over the internet were found to contain undeclared pharmaceutical substances with the main component being sibutramine, an appetite suppressant used in the treatment of obesity. In addition to sibutramine, phenolphthalein and sildenafil were also identified none of which were declared on the box or enclosed information. During our study we were able to identify nine samples that had been contaminated by sibutramine. DART with data directed analysis of the sample using a data directed high low collision energy experiment provides simultaneous intact molecular ion and fragmentation information, while allowing samples to be analysed very rapidly and without the need for complex sample preparation or chromatography. The testing of unlicensed herbal medicines and herbal dietary supplements are vital functions due to the possibility of illegal adulteration and/or contamination and the potential that exists for adverse health effects to unsuspecting consumers.

Evaluating a direct swabbing method for screening pesticides on fruit and vegetable surfaces using direct analysis in real time (DART) coupled to an Exactive benchtop orbitrap mass spectrometer

Crawford, E., & Musselman, B. (2012). Analytical and Bioanalytical Chemistry, 403(10), 2807–2812. doi:10.1007/s00216-012-5853-6

Rapid screening of pesticides present on the surfaces of fruits and vegetables has been facilitated by using a Direct Analysis in Real Time (DART®) open air surface desorption ionization source coupled to an Exactive® high-resolution accurate mass benchtop orbitrap mass spectrometer. The use of cotton and polyester cleaning swabs to collect and retain pesticides for subsequent open air desorption ionization is demonstrated by sampling the surface of various produce to which solutions of pesticides have been applied at levels 10 and 100 times below the tolerance levels established by the United States Environmental Protection Agency (US EPA). Samples analyzed include cherry tomatoes, oranges, peaches and carrots each chosen for their surface characteristics which include: smooth, pitted, fuzzy, and rough respectively. Results from the direct analysis of fungicides on store-bought oranges are also described. In all cases, the swabs were introduced directly into the heated ionizing gas of the DART source resulting in production of protonated pesticide molecules within seconds of sampling. Operation of the orbitrap mass spectrometer at 25,000 full-width half maximum resolution was sufficient to generate high-guality accurate mass data. Stable external mass calibration eliminated the need for addition of standards typically required for mass calibration. thus allowing multiple analyses to be completed without instrument recalibration.

Ambient Ionization–Accurate Mass Spectrometry (AMI-AMS) for the Identification of Nonvisible Set-off in Food-Contact Materials

Bentayeb, K., Ackerman, L. K., & Begley, T. H. (2012). J. Agric. Food Chem., 60(8), 1914–1920. doi:10.1021/jf204456z

Set-off is the unintentional transfer of substances used in printing from the external printed surface of food packaging to the inner, food-contact surface. Ambient ionization-accurate mass spectrometry (AMI-AMS) detected and identified compounds from print set-off not visible to the human eye. AMI mass spectra from inner and outer surfaces of printed and nonprinted food packaging were compared to detect and identify nonvisible set-off components. A protocol to identify unknowns was developed using a custom open-source database of printing inks and food-packaging compounds. The protocol matched print-related food-contact surface ions with the molecular formulas of common ions, isotopes, and fragments of compounds from the database. AMI-AMS was able to detect print set-off and identify seven different compounds. Set-off on the packaging samples was confirmed using gas chromatographic-mass spectrometric (GC-MS) analysis of single-sided solvent extracts. N-Ethyl-2(and 4)-methylbenzenesulfonamide, 2,4-diphenyl-4-methyl-1(and 2)-pentene, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol were present on the food-contact layer at concentrations from 0.21 to 2.7 \pm 1.6 μ g/dm, corresponding to nearly milligram per kilogram concentrations in the packaged food. Other minor set-off compounds were detected only by AMI-AMS, a fast, simple, and thorough technique to detect and identify set-off in food packaging. Set-off is the unintentional transfer of substances used in printing from the external printed surface of food packaging to the inner, food-contact surface. Ambient ionization-accurate mass spectrometry (AMI-AMS) detected and identified compounds from print set-off not visible to the human eye. AMI mass spectra from inner and outer surfaces of printed and nonprinted food packaging were compared to detect and identify nonvisible set-off components. A protocol to identify unknowns was developed using a custom open-source database of printing inks and food-

packaging compounds. The protocol matched printrelated food-contact surface ions with the molecular formulas of common ions, isotopes, and fragments of compounds from the database. AMI-AMS was able to detect print set-off and identify seven different compounds. Set-off on the packaging samples was confirmed using gas chromatographic?mass spectrometric (GC-MS) analysis of single-sided solvent extracts. N-Ethyl-2(and 4)-methylbenzenesulfonamide, 2,4-diphenyl-4-methyl-1(and 2)-pentene, and 2,4,7,9-tetramethyl-5-decyne-4,7-diol were present on the food-contact layer at concentrations from 0.21 to 2.7 ± 1.6 ?g dm?2. corresponding to nearly milligram per kilogram concentrations in the packaged food. Other minor set-off compounds were detected only by AMI-AMS, a fast, simple, and thorough technique to detect and identify set-off in food packaging.

Rapid screening for synthetic antidiabetic drug adulteration in herbal dietary supplements using direct analysis in real time mass spectrometry

Zhou, Z., Zhang, J., Zhang, W., Bai, Y., & Liu, H. (2011). Analyst, 136(12), 2613–2618.

Adulteration of herbal supplements with synthetic drugs is illegal. A rapid and reliable method which utilizes direct analysis in real time mass spectrometry (DART-MS) was developed for the identification of seven synthetic antidiabetic drugs used as adulterants in herbal dietary supplements. The supplement sample was simply extracted with methanol/water by manually shaking several times and directly analyzed using DART-MS. The presence of synthetic drug adulterants was confirmed through the accurate m/z values and MS/MS data obtained via guadruple time of flight mass spectrometry (QTOF MS). Parameters for the DART source were systematically optimized, and the limits of detection (LODs) in herbal supplement matrices were measured. This method was successfully applied to examine five commercial herbal dietary supplements, and two of them proved to be adulterated with metformin without labeling.

Surface swabbing technique for the rapid screening for pesticides using ambient pressure desorption ionization with highresolution mass spectrometry

Edison, S. E., Lin, L. A., Gamble, B. M., Wong, J., & Zhang, K. (2011). Rapid Communications in Mass Spectrometry, 25(1), 127–139. doi:10.1002/rcm.4831

A rapid screening method for pesticides has been developed to promote more efficient processing of produce entering the United States. Foam swabs were used to recover a multiclass mixture of 132 pesticides from the surfaces of grapes, apples, and oranges. The swabs were analyzed using direct analysis in real time (DART) ionization coupled with a high-resolution Exactive Orbitrap[™] mass spectrometer. By using a DART helium temperature gradient from 100-350°C over 3 min, a minimal separation of analytes based on volatility differences was achieved. This, combined with the Exactive's mass resolution of 100 000, allowed the chromatographic step, along with the typical compositing and extraction steps associated with gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/mass spectrometry (LC/MS) approaches, to be eliminated. Detection of 86% of the analytes present was consistently achieved at levels of 2 ng/g (per each apple or orange) and 10 ng/g (per grape). A resolution study was conducted with four pairs of isobaric compounds analyzed at a mass resolution of 100 000. Baseline separation was achieved with analyte ions differing in mass by 25 ppm and analyte ions with a mass difference of 10 ppm were partially resolved. In addition, field samples that had undergone traditional sample preparation using QuEChERS (quick, easy, cheap, rugged, and safe) were analyzed using both LC/MS and DART-MS and the results from the two techniques were found to be comparable in terms of identification of the pesticides present. The use of swabs greatly increased sample throughput by reducing sample preparation and analysis time.

Authentication, Identification, and Quality Control

Authentication of Animal Fats Using Direct Analysis in Real Time (DART) Ionization–Mass Spectrometry and Chemometric Tools

Vaclavik, L., Hrbek, V., Cajka, T., Rohlik, B.-A., Pipek, P., & Hajslova, J. (2011). J. Agric. Food Chem., 59(11), 5919–5926. doi:10.1021/jf200734x

A combination of direct analysis in real time (DART) ionization coupled to time-of-flight mass spectrometry (TOFMS) and chemometrics was used for animal fat (lard and beef tallow) authentication. This novel instrumentation was employed for rapid profiling of triacylglycerols (TAGs) and polar compounds present in fat samples and their mixtures. Additionally, fat isolated from pork, beef, and pork/beef admixtures was analyzed. Mass spectral records were processed by principal component analysis (PCA) and stepwise linear discriminant analysis (LDA). DART-TOFMS profiles of TAGs were found to be more suitable for the purpose of discrimination among the examined fat types as compared to profiles of polar compounds. The LDA model developed using TAG data enabled not only reliable classification of samples representing neat fats but also detection of admixed lard and tallow at adulteration levels of 5 and 10% (w/w), respectively. The presented approach was also successfully applied to minced meat prepared from pork and beef with comparable fat content. Using the DART-TOFMS TAG profiles of fat isolated from meat mixtures, detection of 10% pork added to beef and vice versa was possible. A combination of direct analysis in real time (DART) ionization coupled to time-of-flight mass spectrometry (TOFMS) and chemometrics was used for animal fat (lard and beef tallow) authentication. This novel instrumentation was employed for rapid profiling of triacylglycerols (TAGs) and polar compounds present in fat samples and their mixtures. Additionally, fat isolated from pork, beef, and pork/beef admixtures was analyzed. Mass spectral records were processed by principal component

analysis (PCA) and stepwise linear discriminant analysis (LDA). DART-TOFMS profiles of TAGs were found to be more suitable for the purpose of discrimination among the examined fat types as compared to profiles of polar compounds. The LDA model developed using TAG data enabled not only reliable classification of samples representing neat fats but also detection of admixed lard and tallow at adulteration levels of 5 and 10% (w/w), respectively. The presented approach was also successfully applied to minced meat prepared from pork and beef with comparable fat content. Using the DART-TOFMS TAG profiles of fat isolated from meat mixtures, detection of 10% pork added to beef and vice versa was possible.

Rapid identification of traditional Chinese herbal medicine by direct analysis in real time (DART) mass spectrometry

Wang, Y., Li, C., Huang, L., Liu, L., Guo, Y., Ma, L., & Liu, S. (2014). Analytica Chimica Acta, (0). doi:10.1016/j.aca.2014.06.014

Direct analysis in real time-mass spectrometry (DART-MS) was employed as a novel fast method to identify traditional Chinese herbal medicine (TCHM). In order to obtain high quality mass spectra, the ionization temperature was optimized for every kind of sample. With minimal or no sample pretreatment, major TCHM components, including alkaloids. flavonoids and some ginsenosides, were directly detected within several seconds, while thirteen ginsenosides need derivatization to get good mass spectra. Pseudoginsenoside F11, compound K, protopanaxatriol (PPT) and protopanaxadiol (PPD), for the first time were detected without derivatization. Among five of eight tested Chinese herbal medicines, Rhizoma Corvdalis, Bulbus Fritillariae Thunbergii, Arecae Semen, Ramulus Uncariae Cum Uncis and Scutellariae Radix, were first time identified by DART-MS. In addition, the ionization mechanisms of major herbal components, alkaloids, flavonoids and ginsenosides, were discussed in detail. Our results demonstrated that DART-MS could provide a rapid, reliable and environmental friendly method for the rapid identification of TCHM, and may be applicable to other plants.

Metabolic fingerprinting based on highresolution tandem mass spectrometry: a reliable tool for wine authentication?

Rubert, J., Lacina, O., Fauhl-Hassek, C., & Hajslova, J. (2014). Analytical and Bioanalytical Chemistry. doi:10.1007/s00216-014-7864-y

Ultra-high-performance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry (MS) and an alternative technology represented by direct analysis in real time coupled with guadrupole time-of-flight MS were investigated for metabolic fingerprinting of 343 red and white wine samples. Direct injection of pure wine and an extraction procedure optimized for isolation of polyphenols were used to compare different analytical and data handling strategies. After data processing and data pretreatment, principal component analysis was initially used to explore the data structure. Initially, the unsupervised models revealed a notable clustering according to the grape varieties, and therefore supervised orthogonal partial least squares discriminant analysis models were created and validated for separation of red and white wines according to the grape variety. The validated orthogonal partial least squares discriminant analysis models based on data (ions) recorded in positive ionization mode were able to classify correctly 95 % of samples. In parallel, authentication parameters, such as origin and vintage, were evaluated, and they are discussed. A tentative identification of markers was performed using accurate mass measurement of MS and MS/MS spectra, different software packages and different online libraries. In this way, different flavonol glucosides and polyphenols were identified as wine markers according to the grape varieties.

DART-TOF-MS based metabolomics study for the discrimination analysis of geographical origin of Angelica gigas roots collected from Korea and China

Kim, H., Seo, Y., Park, S., Jeong, S., Kim, M., & Jang, Y. (2014). Metabolomics. doi:10.1007/s11306-014-0671-9

Rapid and efficient identification of the geographical origin of Angelica gigas roots (dang-gui) was performed using DART-TOF-MS (direct analysis in real time-time of flight-mass spectrometry) based metabolomics. As an ambient desorption/ionization technique, DART-TOF-MS can provide soft ionization and rapid analysis of samples with little sample preparation so it has been advantageously applied to high-throughput metabolomics analysis. In order to develop an efficient tool for discriminating, particularly geographical origin of raw herbal medicine, we employed DART-TOF-MS fingerprinting on dang-gui from Korean and Chinese markets. Principal component analysis of DART-TOF-MS fingerprints gave distinctive clustering information among two species of A. gigas and A. sinensis so that we used only A. gigas species for the sequential experiment. Orthogonal projections to latent structures-discriminant analysis of A. gigas samples revealed the separation between samples cultivated in two countries. Major discriminating components were elucidated as decursin/decursinol angelate, unidentified molecular ion of m/z 247 (protonated ions of molecular formula of C14H14O4) and another molecular ion of m/z 432. DART-TOF-MS based chemical fingerprinting with the multivariate analysis of dang-gui was shown to be efficient and accurate way to identify its geographical origin, between Korea and China.

Authentication of milk and milk-based foods by direct analysis in real time ionization– high resolution mass spectrometry (DART– HRMS) technique: A critical assessment

Hrbek, V., Vaclavik, L., Elich, O., & Hajslova, J. (2014). Food Control, 36(1), 138–145. doi:10.1016/j.foodcont.2013.08.003

The potential of direct analysis in real time (DART) ambient ionization technique coupled with high resolution mass spectrometry (HRMS) in authentication of milk and dairy products was critically assessed. In particular case, DART-HRMS was used for several scenarios: (i) discrimination among milks obtained from various farm animal species (cow, goat, and sheep), (ii) discrimination between cows' milk produced in conventional and organic farming, and, (iii) detection of vegetable oil added to a milk-based product (soft cheese). For this purpose, a rapid profiling procedure based on examination of milk/cheese toluene extracts, was implemented. The obtained triacylglycerol (TAG) profiles (mass spectra) were processed with principal component analysis (PCA) and linear discriminant analysis (LDA). Based on LDA model, reliable differentiation of cows' milk samples and goats'/sheep's milk was possible. The DART-HRMS procedure also allowed distinguishing milk mixtures prepared at adulteration level of 50% (v/v). The capability to recognize milk from conventional and organic farming was rather low, poor classification rates of the LDA model were obtained. On the other hand, reliable detection of the presence of vegetable oils (rapeseed, sunflower, and soybean), added to soft cheese at amount as low as 1% (w/w), was possible. Additionally, the quality of added oil in terms of degree of its oxidation could be documented.

Distinguishing wild from cultivated agarwood (Aquilaria spp.) using direct analysis in real time and time of-flight mass spectrometry

Espinoza, E. O., Lancaster, C. A., Kreitals, N. M., Hata, M., Cody, R. B., & Blanchette, R. A. (2014). Rapid Communications in Mass Spectrometry, 28(3), 281–289. doi:10.1002/rcm.6779

It is important for the enforcement of the CITES treaty to determine whether agarwood (a resinous wood produced in Aquilaria and Gyrinops species) seen in trade is from a plantation that was cultivated for sustainable production or was harvested from natural forests which is usually done illegally. METHODS We analyzed wood directly using Direct Analysis in Real Time (DART[™]) ionization coupled with Time-of-Flight Mass Spectrometry (TOFMS). Agarwood was obtained from five countries, and the collection contained over 150 samples. The spectra contained ions from agarwood-specific 5,6,7,8tetrahydro-2-(2-phenylethyl)chromones as well as many other ions. The data was analyzed using either kernel discriminant analysis or kernel principal component analysis. Probability estimates of origin (wild vs cultivated) were assigned to unknown agarwood samples. RESULTS Analysis of the DART-TOFMS data shows that many of the chromones found in cultivated and wild agarwood samples are similar; however, there is a significant difference in particular chromones that can be used for differentiation. In certain instances, the analysis of these chromones also allows inferences to be made as to the country of origin. Mass Mountaineer[™] software provides an estimate of the accuracy of the discriminate model, and an unknown sample can be classified as cultivated or wild. Eleven of the thirteen validation samples (85%) were correctly assigned to either cultivated or wild harvested for their respective geographic provenance. The accuracy of each classification can be estimated by probabilities based on Z scores. CONCLUSIONS The direct analysis of wood for the diagnostic chromones using DART-TOFMS followed by discriminant analysis is sufficiently robust to differentiate wild from cultivated agarwood and provides strong inference for the origin of the agarwood.

Characterization of volatile and semi-volatile compounds in green and fermented leaves of Bergenia crassifolia L. by GC-MS and ID-CUBE DART-HRMS

Chernetsova, E., Shikov, A., Crawford, E., Grashorn, S., Laakso, I., Pozharitskaya, O., ... Morlock, G. (2014). European Journal of Mass Spectrometry, 20(2), 199–205. doi:http://dx.doi.org/10.1255/ejms.1252

Chemical compositions of volatile and semi-volatile components in green and fermented leaves of Bergenia crassifolia L. were studied. Leaf components were identified using gas chromatography with low resolution mass spectrometry and direct analysis in real time (DART) high resolution mass spectrometry with an ID-CUBE ion source. Phytol, nerolidol, geraniol, linalool, αbisabolol. α -bisabololoxide B. α -cadinol. δ -cadinene. α-terpineol, and several other marker compounds of special interest were defined, for which the process of fermentation significantly changed their content in the leaves. Low resolution EI GC-MS and ID-CUBE DART-HRMS were found to be complementary methods, as they provide different information, helpful to increase the confidence of identification.

Application of mixture analysis to crude materials from natural resources (IV)[1(a-c)]: identification of Glycyrrhiza species by direct Analysis in real time mass spectrometry (II).

Fukuda, E., Uesawa, Y., Baba, M., & Okada, Y. (2013). Natural Product Communications, 8(12), 1721–1724.

In order to identify Glycyrrhiza species by chemical fingerprinting, the bark of the roots and stolons of Glycyrrhiza uralensis Fischer and G. glabra Linné were analyzed using DART (Direct Analysis in Real Time)-MS. The characteristic peaks of each species were determined statistically by volcano plot. This summarizes the relationship between the p-values of a statistical test and the magnitude of the difference in values of the samples in the groups. In this experiment, peaks that had a p value <0.05 in the t test and Z2 absolute difference were defined as characteristic. As a result, characteristic peaks of G. uralensis were found at m/z 299, 315, 341, and 369. In contrast, characteristic peaks of G. glabra were found at m/z 323, 325, 337, 339, and 391. In conclusion, we found several characteristic peaks to distinguish G. uralensis and G. glabra by DART-MS using volcano plot. This method can be applied to identify the Glycyrrhiza species.

Rapid determination of 5hydroxymethylfurfural by DART ionization with time-of-flight mass spectrometry

Rajchl, A., Drgová, L., Grégrová, A., Čížková, H., Ševčík, R., & Voldřich, M. (2013). Analytical and Bioanalytical Chemistry, 405(14), 4737–4745. doi:10.1007/s00216-013-6875-4

DART (direct analysis in real time), a novel technique with wide potential for rapid screening analysis, coupled with high-resolution time-of-flight mass spectrometry (TOF-MS) has been used for quantitative analysis of 5-hydroxymethylfurfural (5-HMF), a typical temperature marker of food. The DART/TOF-MS method was optimised and validated. Quantification of 5-HMF was achieved by use of a stable isotope-labelled 5-HMF standard prepared from glucose. Formation of 5-HMF from saccharides, a potential source of overestimation of results, was evaluated. Forty-four real samples (honey and caramelised condensed sweetened milk) and 50 model samples of heated honey were analysed. The possibility of using DART for analysis of heated samples of honey was confirmed. HPLC and DART/TOF-MS methods for determination of 5-HMF were compared. The correlation equation between these methods was DART = 1.0287HPLC + 0.21340, R 2 = 0.9557. The

DART = 1.0287 HPLC + 0.21340, R 2 = 0.9557. The DART/TOF-MS method has been proved to enable efficient and rapid determination of 5-HMF in a variety of food matrices, for example honey and caramel.

Application of direct analysis in real time ionization–mass spectrometry (DART–MS) in chicken meat metabolomics aiming at the retrospective control of feed fraud

Cajka, T., Danhelova, H., Zachariasova, M., Riddellova, K., & Hajslova, J. (2013). Metabolomics, 9(3), 545–557. doi:10.1007/s11306-013-0495-z

Metabolomic fingerprinting enabled by ambient mass spectrometry employing a direct analysis in real time (DART) ion source coupled to a mediumhigh resolution/accurate mass time-of-flight mass spectrometer (TOFMS) was used as a tool for differentiation between chickens fed by feed that contained 5-8 % (w/w) of chicken bone meal (a banned component) and those representing a reference group, i.e. grown otherwise under the same conditions. In the first step, the sample extraction and DART-TOFMS instrumental conditions were optimized to obtain the broadest possible representation of ionizable compounds occurring in the extracts obtained from chicken muscle and feed on which experimental animals were grown. To this end, a simultaneous (all-in-one) extraction procedure was developed employing water and cyclohexane mixture as the extraction solvents. Under these conditions both polar as well as non-polar metabolites were isolated within a single extraction step. In the next step, metabolomic fingerprints of a large set of chicken muscle and feed extracts were acquired. In the final phase, the experimental data were statistically evaluated using principal component analysis and orthogonal partial least squares discriminant analysis. In general, differentiation of chicken muscle according to diet (feed with and without the addition of chicken bone meal) was feasible. Additional experiments conducted after 6 months confirmed applicability of this approach. Correct classification was obtained based on the assessment of polar as well as nonpolar extracts fingerprints. However, the analysis of non-polar extracts showed that the pattern of triacylglycerols is more prone to seasonal variability and/or type of raw materials used during feed preparation which obscures the bone meal impact to some extent.

Detection of Caffeine in Tea, Instant Coffee, Green Tea Beverage, and Soft Drink by Direct Analysis in Real Time (DART) Source Coupled to Single-Quadrupole Mass Spectrometry

Wang, L., Zhao, P., Zhang, F., Bai, A., & Pan, C. (2013). Journal of AOAC International, 96(2), 353– 356. doi:10.5740/jaoacint.12-160

Ambient ionization direct analysis in real time (DART) coupled to single-quadrupole MS (DART-MS) was evaluated for rapid detection of caffeine in commercial samples without chromatographic separation or sample preparation. Four commercial samples were examined: tea, instant coffee, green tea beverage, and soft drink. The response-related parameters were optimized for the DART temperature and MS fragmentor. Under optimal conditions, the molecular ion (M+H)+ was the major ion for identification of caffeine. The results showed that DART-MS is a promising tool for the quick analysis of important marker molecules in commercial samples. Furthermore, this system has demonstrated significant potential for high sample throughput and real-time analysis.

Monitoring tea fermentation/manufacturing by Direct Analysis in Real Time (DART) mass spectrometry

Fraser, K., Lane, G. A., Otter, D. E., Harrison, S. J., Quek, S.-Y., Hemar, Y., & Rasmussen, S. (2013). Food Chemistry, 141(3), 2060–2065. doi:10.1016/j.foodchem.2013.05.054

Factors such as fermentation methods, geographical origin and season can affect the biochemical composition of tea leaves (Camellia sinensis L.). In this study, the biochemical composition of oolong tea during the manufacturing and fermentation process was studied using a non-targeted method utilising ambient ionisation with a direct analysis in real time (DART) ion source and mass spectrometry (MS). Caffeine dominated the positive ionisation spectra throughout the manufacturing process, while the negative ion spectra collected during manufacturing were rich in ions likely to be surface lipids. Correlation analyses on the spectra revealed two volatile compounds tentatively identified as indole and geranic acid, along with ammonium and caffeine clusters/adducts with geranic acid that increased in concentration during the fermentation stages of the process. The tentative identifications were assigned using a combination of DART-iontrap MSn and DART-accurate mass MS1 and MS2 on tea samples and standard compounds. This study highlights the potential of DART-MS to rapidly monitor the progress of complex manufacturing processes such as tea fermentation.

Direct Analysis in Real Time (DART) Ionization as a Tool for Rapid Screening and Characterization of Black Cohosh (Actaea racemosa) by MS Fingerprints

Crawford, E., Goguen, R., LaPointe, J., & Musselman, B. (2013). Planta Med, 79(05), P117. doi:10.1055/s-0033-1336559

Characterization of herbal dietary supplements has increasingly become a focus for regulatory bodies. In this study we have used a Direct Analysis in Real Time (DART) ambient ionization mass spectrometry method to characterize the major ionizable components in Black Cohosh (Actaea racemosa). Analysis of both the raw natural product and several commercial products labeled as containing Black Cohosh yielded wide variation in the mass spectral composition across the products. In order to permit more uniform sampling we choose to investigate guick extraction protocols with 0.1N acid, 0.1N base, and a published method for Black Cohosh sample prep [1]. The DART-MS experiment involves employing a thermal profile method for each extract using different gas temperatures (150 °C, 250 °C, and 350 °C) for desorption ionization and positive/negative ion mass spectrometric detection. Ferulic acid and caffeic acid desorption were optimized at 250 °C in the negative ion mode. Carbohydrates were detected at 150 °C and 250 °C in the positive ion spectra from the raw plant materials; however, they were not detected in all commercial products. The 250 °C positive and negative ion spectra proved to yield a large number of ions and these spectra were designated as the MS Fingerprint data. These MS Fingerprints were subsequently subjected to analysis using a statistical spectral matching program for automated chemometric analysis of the samples for differentiation.

Chemometric Classification of Morphologically Similar Umbelliferae Medicinal Herbs by DART-TOF-MS Fingerprint

Lee, S. M., Kim, H.-J., & Jang, Y. P. (2012). Phytochemical Analysis, 23(5), 508–512. doi:10.1002/pca.2348

Introduction It needs many years of special training to gain expertise on the organoleptic classification of botanical raw materials and, even for those experts, discrimination among Umbelliferae medicinal herbs remains an intricate challenge due to their morphological similarity. Objective To develop a new chemometric classification method using a direct analysis in real time-time of flight-mass spectrometry (DART-TOF-MS) fingerprinting for Umbelliferae medicinal herbs and to provide a platform for its application to the discrimination of other herbal medicines. Methodology Angelica tenuissima, Angelica gigas, Angelica dahurica and Cnidium officinale were chosen for this study and ten samples of each species were purchased from various Korean markets. DART-TOF-MS was employed on powdered raw materials to obtain a chemical fingerprint of each sample and the orthogonal partial-least squares method in discriminant analysis (OPLS-DA) was used for multivariate analysis. Results All samples of collected species were successfully discriminated from each other according to their characteristic DART-TOF-MS fingerprint. Decursin (or decursinol angelate) and byakangelicol were identified as marker molecules for Angelica gigas and A. dahurica, respectively. Using the OPLS method for discriminant analysis, Angelica tenuissima and Cnidium officinale were clearly separated into two groups. Angelica tenuissima was characterised by the presence of ligustilide and unidentified molecular ions of m/z 239 and 283, while senkyunolide A together with signals with m/z 387 and 389 were the marker compounds for Cnidium officinale. Conclusion Elaborating with chemoinformatics, DART-TOF-MS fingerprinting with chemoinformatic tools results in a powerful method for the classification of morphologically similar Umbelliferae medicinal herbs and quality control of medicinal

herbal products, including the extracts of these crude drugs.

Direct Analysis in Real Time by Mass Spectrometric Technique for Determining the Variation in Metabolite Profiles of Cinnamomum tamala Nees and Eberm Genotypes

Singh, V., Gupta, A. K., Singh, S. P., & Kumar, A. (2012). The Scientific World Journal, 2012. doi:10.1100/2012/549265

Cinnamomum tamala Nees & Eberm. is an important traditional medicinal plant, mentioned in various ancient literatures such as Ayurveda. Several of its medicinal properties have recently been proved. To characterize diversity in terms of metabolite profiles of Cinnamomum tamala Nees and Eberm genotypes, a newly emerging mass spectral ionization technique direct time in real time (DART) is very helpful. The DART ion source has been used to analyze an extremely wide range of phytochemicals present in leaves of Cinnamomum tamala. Ten genotypes were assessed for the presence of different phytochemicals. Phytochemical analysis showed the presence of mainly terpenes and phenols. These constituents vary in the different genotypes of Cinnamomum tamala. Principal component analysis has also been employed to analyze the DART data of these Cinnamomum genotypes. The result shows that the genotype of Cinnamomum tamala could be differentiated using DART MS data. The active components present in Cinnamomum tamala may be contributing significantly to high amount of antioxidant property of leaves and, in turn, conditional effects for diabetic patients.

Rapid control of Chinese star anise fruits and teas for neurotoxic anisatin by Direct Analysis in Real Time (DART) high resolution mass spectrometry

Shen, Y., van Beek, T. A., Claassen, F. W., Zuilhof, H., Chen, B., & Nielen, M. W. F. (2012). Journal of Chromatography A, 1259, 179–186. doi:10.1016/j.chroma.2012.03.058

After ingestion, products containing Chinese star anise (Illicium verum) contaminated or adulterated with Japanese star anise (Illicium anisatum) or other Illicium species, can cause epilepsy, hallucinations, and nausea due to the rare neurotoxic sesquiterpene dilactone anisatin that is present in Japanese star anise. Thus a rapid, simple and unambiguous method for distinguishing between the morphologically similar Chinese star anise and toxic Japanese star anise is important for food safety issues. Direct Analysis in Real Time (DART) ambient ionisation coupled with orbitrap high resolution mass spectrometry allowed the recording of mass spectra of anisatin in solid star anise fruits in seconds without any prior sample pretreatment. Spectra could be obtained in both positive $([M+NH_4]^+ \text{ at } m/z)$ 346.1496, $C_{15}H_{24}NO_8$) and negative mode ([M-H]⁻ at m/z 327.1074, $C_{15}H_{19}O_8$) and gave the same outcome provided a mass resolution of at least 27,000 is available. The anisatin signal was typically 1000 times larger in Japanese star anise than in Chinese star anise thus allowing an unequivocal gualitative determination. Herbal teas containing star anise fragments too small to be visually recognised, could be analysed by preparing a tea in 6min and subsequently sampling $\sim 2\mu L$ of tea on a glass rod. None of the 8 investigated retail teas contained significant quantities of anisatin. Spiking a complex herbal tea containing Chinese star anise with an equally concentrated tea prepared from Japanese star anise provided a linear calibration curve (R2≥0.995) after normalising on a native constituent of Chinese star anise (standard addition method). This showed that adulteration down to 1% (w/w) is still measurable. Compared with existing PCR, TLC, GC-MS and HPLC-ESI-MS/MS procedures, the proposed DART-HRMS procedure is faster and simpler and moreover measures the actual biotoxin.

Rapid classification of White Oak (Quercus alba) and Northern Red Oak (Quercus rubra) by using pyrolysis direct analysis in real time (DART[™]) and time-of-flight mass spectrometry

Cody, R. B., Dane, A. J., Dawson-Andoh, B., Adedipe, E. O., & Nkansah, K. (2012). Journal of Analytical and Applied Pyrolysis, 95(0), 134–137. doi:10.1016/j.jaap.2012.01.018

Thirty-four samples of Red Oak (Quercus rubra) and fifty samples of White Oak (Quercus alba) were analyzed by pyrolytic direct analysis in real time (DART) ionization coupled with time-of-flight (TOF) mass spectrometry. Although significant differences were not observed in the positive-ion mass spectra, the negative-ion mass spectra showed clear differences. Principal component analysis (PCA) and linear discriminant analysis (LDA) were calculated for the relative abundances of 11 peaks in the negative-ion mass spectra including peaks tentatively assigned as representing deprotonated acetic, malic, gallic, dimethoxycinnamic, and ellagic acids. Leave one out cross validation (LOOCV) was 100% successful in classifying the samples for both PCA and LDA.

Rapid quality assessment of Radix Aconiti Preparata using direct analysis in real time (DART) mass spectrometry

Zhu, H., Wang, C., Qi, Y., Song, F., Liu, Z., & Liu, S. (2012). Analytica Chimica Acta, 752, 69–77. doi:10.1016/j.aca.2012.09.018

This study presents a novel and rapid method to identify chemical markers for the quality control of Radix Aconiti Preparata, a world widely used traditional herbal medicine. In the method, the samples with a fast extraction procedure were analyzed using direct analysis in real time mass spectrometry (DART MS) combined with multivariate data analysis. At present, the quality assessment approach of Radix Aconiti Preparata was based on the two processing methods recorded in Chinese Pharmacopoeia for the purpose of reducing the toxicity of Radix Aconiti and ensuring its clinical therapeutic efficacy. In order to ensure the safety and effectivity in clinical use, the processing degree of Radix Aconiti should be well controlled and assessed. In the paper, hierarchical cluster analysis and principal component analysis were performed to evaluate the DART MS data of Radix Aconiti Preparata samples in different processing times. The results showed that the well processed Radix Aconiti Preparata, ungualified processed and the raw Radix Aconiti could be clustered reasonably corresponding to their constituents. The loading plot shows that the main chemical markers having the most influence on the discrimination amongst the gualified and ungualified samples were mainly some monoester diterpenoid aconitines and diester diterpenoid aconitines, i.e. benzoylmesaconine, hypaconitine, mesaconitine, neoline, benzoylhypaconine, benzoylaconine, fuziline, aconitine and 10-OHmesaconitine. The established DART MS approach in combination with multivariate data analysis provides a very flexible and reliable method for guality assessment of toxic herbal medicine.

Chemical Analysis and Research Applications

Evaluation of the Oxidation of Rice Husks with Sodium Hypochlorite Using Gas Chromatography-Mass Spectrometry and Direct Analysis in Real Time-Mass Spectrometry

Wang, S.-Z., Fan, X., Zheng, A.-L., Lu, Y., Wei, X.-Y., Zhao, Y.-P., Liu, D.-Y. (2013). Analytical Letters, 47(1), 77–90. doi:10.1080/00032719.2013.831425

Rice husk powder was oxidized in aqueous sodium hypochlorite solution under mild conditions with different reaction times. Fourier transform infrared spectroscopy, gas chromatography-mass spectrometry (GC-MS), and direct analysis in real time-mass spectrometry (DART-MS) were used to analyze the oxidation products. Results showed that oxidation was a feasible way to depolymerize the macromolecules in the biomass and convert hydroxyl groups to carboxyl groups. In total, 113 organic compounds in oxidation products with molecular mass less than 500 Da were identified using GC-MS. As an ambient ionization technique, DART-MS was applied to the determination of biomass derivatives and revealed mass distribution and molecular structure information for the rice husk oxidation products.

Rapid monitoring of heat-accelerated reactions in vegetable oils using direct analysis in real time ionization coupled with high resolution mass spectrometry

Vaclavik, L., Belkova, B., Reblova, Z., Riddellova, K., & Hajslova, J. (2013). Food Chemistry, 138(4), 2312–2320. doi:10.1016/j.foodchem.2012.12.019

Transmission-mode direct analysis in real time ionization coupled with high resolution mass spectrometry (TM-DART-HRMS) was used to monitor chemical changes in various vegetable oils (olive, rapeseed, soybean and sunflower oil) during their thermally-induced oxidation. This novel instrumental approach enabled rapid fingerprinting of examined samples and detection of numerous sample components, such as triacylglycerols (TAGs), phytosterols, free fatty acids (FFA), and their respective oxidation products. Mass spectra obtained from DART were processed with the use of principal component analysis (PCA) in order to assess the compositional differences between heated and non-heated samples. Good correlation was observed between the normalized intensities of the pre-selected ion corresponding to mono-oxidized TAG and 'classic' criterion represented by the levels of TAG polymers determined by high performancesize exclusion chromatography with refractometric detection (HP-SEC-RID).

Evaluation of direct analysis in real time ionization–mass spectrometry (DART–MS) in fish metabolomics aimed to assess the response to dietary supplementation

Cajka, T., Danhelova, H., Vavrecka, A., Riddellova, K., Kocourek, V., Vacha, F., & Hajslova, J. (2013). Talanta, 115, 263–270. doi:10.1016/j.talanta.2013.04.025

Ambient mass spectrometry employing a direct analysis in real time (DART) ion source coupled to a medium-high resolution/accurate mass time-of-flight mass spectrometer (TOFMS) was used as a rapid tool for metabolomic fingerprinting to study the effects of supplemental feeding with cereals (triticale) on the composition of muscle metabolites of common carp (Cyprinus carpio L.). First, the sample extraction and DART-TOFMS instrumental conditions were optimized to obtain the broadest possible representation of ionizable compounds occurring in the extracts obtained from common carp muscle. To this end, a simultaneous (all-in-one) extraction procedure was developed employing water and cyclohexane mixture as the extraction solvents. Under these conditions both polar as well as non-polar metabolites were isolated within a single extraction step. Next, the metabolomic fingerprints (mass spectra) of a large set of common carp muscle extracts were acquired. Finally, the experimental data were statistically evaluated using principal component analysis (PCA) and orthogonal partial least squares discriminant analysis (OPLS-DA). Using this approach, differentiation of common carp muscle in response to dietary supplementation (feeding with and without cereals) was feasible. Correct classification was obtained based on the assessment of polar and as well as non-polar extracts fingerprints. The current study showed that DART-TOFMS metabolomic fingerprinting represents a rapid and powerful analytical strategy enabling differentiation of common carp muscles according to feeding history by recording metabolomic fingerprints of ionizable components under the conditions of ambient MS.

DART MS based chemical profiling for therapeutic potential of Piper betle landraces.

Bajpai, V., Pandey, R., Negi, M., Kumar, N., & Kumar, B. (2012). Natural Product Communications, 7(12), 1627–1629.

Piper betle Linn. leaves are traditionally used as a folk medicine in India and other Asiatic countries. Twenty-one P. betle landraces were analyzed using a Direct Analysis in Real Time (DART) mass spectral technique and evaluated on the basis of molecules detected in the leaves. Clustering of landraces based on three well known biologically active phenols (m/z 151,165,193) showed two broad groups with high and low phenol contents suggesting differences in their therapeutic potential. Findings of this study could be useful in rapid screening of the landraces for determining their medicinal potential and optimum utilization of the bioresource.

Estimation of camptothecin and pharmacological evaluation of Ophiorrhiza prostrata D. Don and Ophiorrhiza mungos L.

Krishnakumar, G., Rameshkumar, K., Srinivas, P., Satheeshkumar, K., & Krishnan, P. (2012). Asian Pacific Journal of Tropical Biomedicine, 2(2, Supplement), S727–S731. doi:10.1016/S2221-1691(12)60304-9

Objective To carry out the qualitative and quantitative evaluation of camptothecin, estimation of total phenolic compounds and evaluation of in vitro antioxidant activity and cytotoxic activity of Ophiorrhiza prostrata and Ophiorrhiza mungos. Methods Direct Analysis in Real Time- Mass Spectrometry (DART-MS) was employed for the detection of camptothecin in the Ophiorrhiza species, while high performance thin layer chromatography (HPTLC) was used for the estimation of camptothecin. Total phenolic compounds were estimated by modified Folins-Ciocalteu's reagent method. Antioxidant activity was evaluated through DPPH radical, hydroxyl radical, superoxide radical scavenging assays and reducing power assay. The cytotoxicity evaluation was performed using MTT assay on MCF-7 cell lines. Results The presence of camptothecin was confirmed in both the species by the [M++H] peak at 349 by DART-MS analysis. Camptothecin content was estimated as 1.47 µg/gm (dry wt) in O. prostrata and 188.60 µg/gm (dry wt) in O. mungos using HPTLC method. The moderate in vitro antioxidant activities of the methanol extracts corroborates with the low content of phenolic compounds in O. prostrata (9.88 GAE mg/g) and O. mungos (12.73 GAE mg/g). The methanol extract of O. prostrata exhibited remarkable cytotoxicity on human breast cancer cell lines (MCF-7), with IC50 value 1.10µg/mL compared to O. mungos (3.48µg/mL) and standard camptothecin (3.51µg/mL). Conclusions The application of DART-MS proved to be a simple and rapid technique for the detection of camptothecin in Ophiorrhiza species. The higher cytotoxicity for O. prostrata, despite the low content of camptothecin suggests the presence of other potential cytotoxic compounds in O. prostrata.

Mass spectrometry-based metabolomic fingerprinting for screening cold tolerance in Arabidopsis thaliana accessions

Vaclavik, L., Mishra, A., Mishra, K., & Hajslova, J. (2013). Analytical and Bioanalytical Chemistry, 405(8), 2671–2683. doi:10.1007/s00216-012-6692-1

The availability of rapid and reliable tools for monitoring of plants' cold tolerance is a prerequisite for research aimed at breeding of cold-tolerant crop plants. Therefore, we have tested the capacity of metabolomics-based methods employing ultra-highperformance liquid chromatography (UHPLC)-mass spectrometry and direct analysis in real time-mass spectrometry for high-throughput screening of cold tolerance in eight differentially cold-tolerant accessions of Arabidopsis thaliana. Metabolomic fingerprinting of leaf tissues was performed in methanolic extracts for (1) 6-week-old nonacclimated (NAC) plants grown at room temperature, (2) NAC plants cold-acclimated (ACC) at 4 °C for 2 weeks, and (3) cold-acclimated plants given subzero-temperature treatments by slow cooling at -4 °C for 8 h. The generated chromatograms and mass spectra were processed with the use of multivariate statistical analysis employing principal component analysis (PCA) and linear discriminant analysis. The PCA of metabolomic fingerprints classified the investigated A. thaliana accessions into three categories with low, intermediate, and high cold tolerance for both the cold-acclimated and the subzero-temperature-treated plants. This indicates the potential application of metabolomics-based fingerprinting for measuring cold tolerance in the cold-acclimated state, i.e., without treating plants at freezing temperatures that is required by currently available methods. Furthermore, we employed UHPLC coupled to the quadrupole-time-of-flight mass spectrometry to identify characteristic metabolites in ACC state and found the abundance of gluconapin and flavon-3-ol glycosides, respectively, in the cold-sensitive and the coldtolerant accessions.

Study of the distribution profile of piperidine alkaloids in various parts of Prosopis juliflora by the application of Direct Analysis in Real Time Mass Spectrometry (DART-MS)

Singh, S., & Verma, S. (2012). Natural Products and Bioprospecting, 2(5), 206–209.

Direct Analysis in Real Time Mass Spectrometry (DART-MS) was applied to identify and study the distribution profile of piperidine alkaloids in different parts of Prosopis juliflora, without isolation and separation of the compounds by standard chromatographic techniques. With the help of DART-MS, chemical fingerprint of raw plant parts were generated, which revealed the presence of piperidine alkaloids in leaf, pod and flower. A comparative study of the distribution pattern, showed variation in the presence and distribution of these alkaloids in various parts of P. juliflora. The leaves and pod displayed the largest alkaloid pattern with a total of 12 different alkaloids in each part, whereas only 4 alkaloids were present in flower. Alkaloids: julifloridine, prosopine, prosopinine and prosafrinine were ubiquitously distributed in all the alkaloid rich plant parts. Juliprosopine was preeminet alkaloid in leaf, whereas pod and flower displayed copious amounts of julifloridine.

Optimization of direct analysis in real time (DART) linear ion trap parameters for the detection and quantitation of glucose

Saang'onyo, D. S., & Smith, D. L. (2012). Rapid Communications in Mass Spectrometry, 26(3), 385– 391. doi:10.1002/rcm.5316

Presented here are findings for the development and optimization of a simple, high-throughput, and rapid method for the analysis of glucose. Because the applications of glucose and other six-carbon sugars is a growing field of interest especially in the production of biofuels, an efficient and rapid method for their quantitation from lignocelluloses is necessary. Glucose was analyzed using direct analysis in real time (DART) ionization and formed adducts (along with fragmentation) were observed with a linear ion trap (LIT) mass spectrometer. Since DART can be considered a complex thermal desorption ionization process, an optimization study of the helium gas temperature and introduction into the ionization region was performed. It was observed these parameters have a significant effect on the overall signal intensity as well as the signalto-noise ratios in DART mass spectra. Using these optimized parameters, a set of different glucose concentrations (ranging from 10 to 3000 µM) were analyzed and used to determine a linear dynamic range (with the use of an internal standard). The analysis of the samples was done with minimal sample preparation and found to be reproducible on different days.

Analysis of isoflavones in soybeans employing direct analysis in real-time ionization–high-resolution mass spectrometry

Lojza, J., Cajka, T., Schulzova, V., Riddellova, K., & Hajslova, J. (2012). Journal of Separation Science, 35(3), 476–481. doi:10.1002/jssc.201100882

A direct analysis in real-time (DART) ion source coupled to a high-resolution orbitrap mass spectrometer was used for the quantitative analysis of isoflavones isolated from soybeans. For the isolation of genistein, daidzein, glycitein, and their respective acetyl, malonyl, and glucoside forms, an extraction employing 80% agueous MeOH enhanced by sonication was used. As far as the total isoflavones (expressed as aglycones) were to be determined, an acid hydrolysis with 80% aqueous EtOH and refluxing had to be employed, while in the latter case a good agreement of the results with the data generated by the UHPLC-orbitrap MS method was achieved, in the case of the analysis of nonhydrolyzed extracts, some overestimation of the results as compared with those generated by UHPLC-orbitrap MS was observed. A careful investigation of this phenomenon showed that the free aglycones originated from the conjugated forms of isoflavones in the DART ion source, thus contributing significantly to the "free" genistein/daidzein/glycitein signals during the DART analysis. Good recoveries (95-102%) and repeatabilities (RSD: 7-15%) were obtained at the spiking levels of 0.5, 1, and 0.05 g/kg, for daidzein, genistein, and glycitein, respectively. The limits of detection estimated for the respective analytes were 5 mg/kg.

Confined direct analysis in real time ion source and its applications in analysis of volatile organic compounds of Citrus limon (lemon) and Allium cepa (onion)

Li, Y. (2012). Rapid Communications in Mass Spectrometry, 26(10), 1194–1202. doi:10.1002/rcm.6217

The DART (direct analysis in real time) ion source is a novel atmospheric pressure ionization technique that enables efficient ionization of gases, liquids and solids with high throughput. A major limit to its wider application in the analysis of gases is its poor detection sensitivity caused by open-air sampling. In this study, a confined interface between the DART ion source outlet and mass spectrometer sampling orifice was developed, where the plasma generated by the atmospheric pressure glow discharge collides and ionizes gas-phase molecules in a Tee-shaped flow tube instead of in open air. It leads to significant increase of collision reaction probability between high energy metastable molecules and analytes. The experimental results show that the ionization efficiency was increased at least by two orders of magnitude. This technique was then applied in the real time analysis of volatile organic compounds (VOCs) of Citrus Limon (lemon) and wounded Allium Cepa (onion). The confined DART ion source was proved to be a powerful tool for the studies of plant metabolomics.

Evaluating agarwood products for 2-(2phenylethyl)chromones using direct analysis in real time time-of-flight mass spectrometry

Lancaster, C., & Espinoza, E. (2012). Rapid Communications in Mass Spectrometry, 26(23), 2649–2656. doi:10.1002/rcm.6388

RATIONALE Agarwood is the resinous material harvested from threatened Aguilaria species. We investigated how many protonated 2-(2phenylethyl)chromone ions were sufficient to make an accurate identification of agarwood. Analysis of 125 reference samples was carried out by direct analysis in real time time-of-flight mass spectrometry (DART-TOFMS). The identification criteria developed were applied to commercial samples. METHODS We developed a technique that uses DART-TOFMS to detect 2-(2phenylethyl)chromones. Additionally, we developed a set of criteria to infer the presence of Aquilaria in commercial samples of wood chips, sawdust, incense and liquids. Additionally, we examined other fragrant woods to determine if they contained a chemical profile that could be falsely identified as agarwood. RESULTS Analysis of reference and commercial samples (n = 151) established that DART-TOFMS provides reproducible mass spectra that are useful for inferring the genus of suspected agarwood samples. We identified 17 ions which were useful for authenticating agarwood. Comparison of the number of chromone ions detected by direct analyses of dry wood chips versus eluent analysis of methanol-extracted wood showed that results were similar. Lastly, analysis of 25 scented woods of other species did not give false positive results. CONCLUSIONS Reliable criteria for inferring agarwood include the presence of diagnostic ions, m/z 319.118 or 349.129, in addition to ten or more ions characteristic of 2-(2phenylethyl)chromones. Wood anatomists challenged with difficult morphological identifications can use this tool to assist in their analyses.

Rapid analysis of caffeine in various coffee samples employing direct analysis in realtime ionization-high-resolution mass spectrometry

Danhelova, H., Hradecky, J., Prinosilova, S., Cajka, T., Riddellova, K., Vaclavik, L., & Hajslova, J. (2012). Analytical and Bioanalytical Chemistry, 403(10), 2883–2889.

The development and use of a fast method employing a direct analysis in real time (DART) ion source coupled to high-resolution time-of-flight mass spectrometry (TOFMS) for the quantitative analysis of caffeine in various coffee samples has been demonstrated in this study. A simple sample extraction procedure employing hot water was followed by direct, high-throughput (<1 min per run) examination of the extracts spread on a glass rod under optimized conditions of ambient mass spectrometry, without any prior chromatographic separation. For quantification of caffeine using DART-TOFMS, an external calibration was used. Isotopically labeled caffeine was used to compensate for the variations of the ion intensities of caffeine signal. Recoveries of the DART-TOFMS method were 97% for instant coffee at the spiking levels of 20 and 60 mg/g, respectively, while for roasted ground coffee, the obtained values were 106% and 107% at the spiking levels of 10 and 30 mg/g, respectively. The repeatability of the whole analytical procedure (expressed as relative standard deviation, RSD, %) was &It;5% for all tested spiking levels and matrices. Since the linearity range of the method was relatively narrow (two orders of magnitude), an optimization of sample dilution prior the DART-TOFMS measurement to avoid saturation of the detector was needed.

Analytical strategies for controlling polysorbate-based nanomicelles in fruit juice

Krtkova, V., Schulzova, V., Lacina, O., Hrbek, V., Tomaniova, M., & Hajslova, J. (2014). Analytical and Bioanalytical Chemistry, 406(16), 3909–3918. doi:10.1007/s00216-014-7823-7

This study focused on the detection and quantification of organic micelle-type nanoparticles (NPs) with polysorbate components (polysorbate 20 and polysorbate 80) in their micelle shells that could be used to load biologically active compounds into fruit juice. Several advanced analytical techniques were applied in the stepwise method development strategy used. In the first phase, a system consisting of ultrahigh-performance liquid chromatography employing a size exclusion column coupled with an evaporative light scattering detector (UHPLC-SEC-ELSD) was used for the fractionation of micelle assemblies from other, lower molecular weight sample components. The limit of detection (LoD) of these polysorbate micelles in spiked apple juice was 500 µg mL-1. After this screening step, mass spectrometric (MS) detection was utilized to confirm the presence of polysorbates in the detected micelles. Two alternative MS techniques were tested: (i) ambient high-resolution mass spectrometry employing a direct analysis in real time ion source coupled with an Orbitrap MS analyzer (DART-Orbitrap MS) enabled fast and simple detection of the polysorbates present in the samples, with a lowest calibration level (LCL) of 1000 µg mL-1; (ii) ultrahigh-performance reversedphase liquid chromatography coupled with highresolution time-of-flight mass spectrometry (UHPLC-HRTOF-MS) provided highly selective and sensitive detection and quantification of polysorbates with an LCL of 0.5 µg mL-1.

ID-CUBE direct analysis in real time highresolution mass spectrometry and its capabilities in the identification of phenolic components from the green leaves of Bergenia crassifolia L.

Chernetsova, E. S., Crawford, E. A., Shikov, A. N., Pozharitskaya, O. N., Makarov, V. G., & Morlock, G. E. (2012). Rapid Communications in Mass Spectrometry, 26(11), 1329–1337. doi:10.1002/rcm.6226

RATIONALE Bergenia crassifolia is a plant widely used in herbal medicine. Its chemical composition has been little studied, and no studies using highresolution mass spectrometry (HRMS) have been performed. Its phenolic components are of particular interest, due to the interest in such compounds in medicine and cosmetics. The ID-CUBE, a simplified Direct Analysis in Real Time (DART) ion source, suitable for the fast MS analysis of liquids without complex sample preparation, offers a new method of studying extracts of such plant. Coupling the ID-CUBE with a high-resolution mass spectrometer can provide identification of extract components. METHODS Mass spectral conditions were optimized for model solutions of the flavonoid naringenin and used for the identification of phenolic compounds in green leaves extracts of Bergenia crassifolia. OpenSpot sample cards with a metal grid surface were used for sample introduction into the ID-CUBE ion source on an Obitrap mass spectrometer. The samples were applied as 5-µL aliquots of the extract onto the metal grid of the card. Sample ionization was stimulated in the ion source within 20 s by applying an electric current to the metal grid to thermally desorb the analytes into the gas flow of metastable helium atoms from the ID-CUBE. RESULTS Elemental compositions were assigned to abundant ions in the mass spectra of the extracts. The major phenolic components were confirmed by their [M–H]– ions. Thirty-six other marker ions were found, and elemental compositions were suggested for 30% of them, based on a search for compounds found in herbal extracts. CONCLUSIONS The ID-CUBE–Orbitrap MS coupling allowed the rapid accurate mass determination of the phenolic components (and other compounds) in herbal extracts. Higher confidence in component

identification could be provided by using additional structural elucidation methods, including tandem mass spectrometry (MS/MS), and this will be the focus of future studies.

Assessing the capabilities of direct analysis in real time mass spectrometry for 5hydroxymethylfurfural quantitation in honey

Chernetsova, E. S., & Morlock, G. E. (2012). International Journal of Mass Spectrometry, 314(0), 22–32. doi:10.1016/j.ijms.2012.01.012

The limitations of direct analysis in real time mass spectrometry (DART-MS) were shown with the example of 5-hydroxymethylfurfural (HMF) quantitation in honey. An accurate analyte quantitation was impossible because the carbohydrate matrix partially degraded to the analyte in the ionization region. However, at a decreased DART temperature of 150°C, the DART-MS screening was possible using two spiked reference samples. The influence of instrumental parameters on the composition of the DART mass spectra for HMF and carbohydrates was investigated. Also, first data on scanning surface analysis with DART-MS were obtained giving rise for further studies in this direction.

DART-MS

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- . Dietary Supplements