Food Safety and Quality

Publications and Abstracts
2008-2011

DART MS
Detect Adulterants and Contaminants
Screen for Pesticide Residues
Authenticate Raw Materials and Finished Products
# Table of Contents

Surface swabbing technique for the rapid screening for pesticides using ambient pressure desorption ionization with high-resolution mass spectrometry........................................4

Rapid screening for synthetic antidiabetic drug adulteration in herbal dietary supplements using direct analysis in real time mass spectrometry........................................4

Authentication of Animal Fats Using Direct Analysis in Real Time (DART) Ionization-Mass Spectrometry and Chemometric Tools ........................................................................5

Quantitative analysis of major dibenzocyclooctane lignans in schisandrae fructus by online TLC-DART-MS ........................................................................................................5

Analysis of multiple mycotoxins in cereals under ambient conditions using direct analysis in real time (DART) ionization coupled to high resolution mass spectrometry ........................................................................................................9

Selective ionization of melamine in powdered milk by using argon direct analysis in real time (DART) mass spectrometry. ..................................................................................................................9

Rapid identification of additives in poly(vinyl chloride) lid gaskets by direct analysis in real time ionisation and single-quadrupole mass spectrometry.................................................10

Release kinetics of actives from chewing gums into saliva monitored by direct analysis in real time mass spectrometry..................................................................................................................10

Applications of direct analysis in real time mass spectrometry (DART-MS) in Allium chemistry. (Z)-butanethial S-oxide and 1-butenyl thiosulfimates and their S-(E)-1-butenylcysteine S-oxide precursor from Allium siculum. ........................................................................11

Profiling of Piper betle Linn. cultivars by direct analysis in real time mass spectrometric technique .................................................................................................................................11

Allium chemistry: Use of new instrumental techniques to “see” reactive organosulfur species formed upon crushing garlic and onion .................................................................12

Ambient mass spectrometry employing direct analysis in real time (DART) ion source for olive oil quality and authenticity assessment.................................................................12

Assessing direct analysis in real time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging .......................................................................................13

Direct analysis of curcumin in turmeric by DART-MS ..............................................................................13

Temperature-dependent release of volatile organic compounds of eucalypts by direct analysis in real time (DART) mass spectrometry .................................................................14
Pro-inflammatory enzymes, cyclooxygenase 1, cyclooxygenase 2, and 5-lipooxygenase, inhibited by stabilized rice bran extracts. .........................................................14

Elderberry flavonoids bind to and prevent H1N1 infection in vitro. .................................15

Identification of active ingredients in dietary supplements using non-destructive mass spectrometry and liquid chromatography–mass spectrometry.................................15

Control of Strobilurin Fungicides in Wheat Using Direct Analysis in Real Time Accurate Time-of-Flight and Desorption Electrospray Ionization Linear Ion Trap Mass Spectrometry .................................................................16

Direct analysis in real time–time-of-flight mass spectrometry: Analysis of pesticide residues and environmental contaminants.................................................................16

Analysis of hairy root culture of Rauvolfia serpentina using direct analysis in real time mass spectrometric technique.................................................................17

GC–TOF-MS and DART–TOF-MS: Challenges in the Analysis of Soft Drinks ...........17

Expression of tropane alkaloids in the hairy root culture of Atropa acuminata substantiated by DART mass spectrometric technique...........................................18

Pharmacokinetics of Cyanidin and Anti-Influenza Phytonutrients in an Elder Berry Extract Determined by LC-MS and DART TOF-MS ..........................18
Surface swabbing technique for the rapid screening for pesticides using ambient pressure desorption ionization with high-resolution mass spectrometry

Edison, S. E.; Lin, L. A.; Gamble, B. M.; Wong, J.; Zhang, K.

Food and Drug Administration, Forensic Chemistry Center, Cincinnati, OH, USA.


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 2ng/g (per each apple or orange) and 10ng/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 25ppm and analyte ions with a mass difference of 10ppm 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.

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.

Beijing National Laboratory for Molecular Sciences, Institute of Analytical Chemistry, College of Chemistry and Molecular Engineering, Peking University, China.


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 accurate m/z values and MS/MS data obtained via quadruple 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.
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.

Institute of Chemical Technology, Prague, Technicka 3, 16628 Prague 6, Czech Republic.


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.

Quantitative analysis of major dibenzocyclooctane lignans in schisandrae fructus by online TLC-DART-MS

Kim, H.J.; Oh, M.S.; Hong, J.; Jang, Y.P.

Kyung Hee East–West Pharmaceutical Research Institute, College of Pharmacy, Kyung Hee University, Seoul 130-701, Korea


Introduction – Direct analysis in real time (DART) ion source is a powerful ionising technique for the quick and easy detection of various organic molecules without any sample preparation steps, but the lack of quantitation capacity limits its extensive use in the field of phytochemical analysis.

Objective – To improvise a new system which utilize DART-MS as a hyphenated detector for quantitation.

Methodology – A total extract of Schisandra chinensis fruit was analyzed on a TLC plate and three major lignan compounds were quantitated by three different methods of UV densitometry, TLC-DART-MS and HPLC-UV to compare the efficiency of each method. To introduce the TLC plate into the DART ion source at a constant velocity, a syringe pump was employed. The DART-MS total ion current chromatogram was recorded for the entire TLC plate. The concentration of each lignan compound was calculated from the calibration curve established with standard compound.

Results – Gomisin A, gomisin N and schisandrin were well separated on a silica-coated TLC plate and the specific ion current chromatograms were successfully acquired from the TLC-DART-MS system. The TLC-DART-MS system for the quantitation of natural products showed better linearity and specificity than TLC densitometry, and consumed less time and solvent than conventional HPLC method.

Conclusion – A hyphenated system for the quantitation of phytochemicals from crude herbal drugs was successfully established. This system was shown to have a powerful analytical capacity for the prompt and efficient quantitation of natural products from crude drugs.
Epiafzelechin from the Root Bark of Cassia sieberiana: Detection by DART Mass Spectrometry, Spectroscopic Characterization, and Antioxidant Properties

Kpegba, K.; Agbonon, A.; Petrovic, A.G.; Amouzou, E.; Gbeassor, M.; Proni, G.; Nesnas, N.

Bioorganic Laboratory, Department of Chemistry, Florida Institute of Technology, Melbourne, Florida 32901, United States
Department of Pharmacology and ‡Department of Chemistry, Université de Lom, Togo, West Africa
Department of Chemistry, Columbia University, New York, New York 10027, United States
Science Department, John Jay College of Criminal Justice, New York, New York 10019, United States


The root bark of Cassia sieberiana was analyzed using direct analysis in real time mass spectrometry, and a main flavonoid component with an [M + H]+ mass of 275 was identified. The flavonoid, epiafzelechin, was isolated and fully characterized with the concerted use of NMR spectroscopy, circular dichroism, and optical rotation. Electronic circular dichroism and optical rotation TDDFT calculations were also performed, and their agreement with the experimental results confirmed the enantiomeric identity of the isolated natural product. The antioxidant activity of the compound was also investigated.

Precursors and Formation of Pyrithione and Other Pyridyl-Containing Sulfur Compounds in Drumstick Onion, Allium stipitatum

Kubec, R.; Krejcová, P.; Simek, P.; Vaclavík, L.; Hajslova, J.; Schraml, J.

Department of Applied Chemistry, University of South Bohemia, Branišovsk 31, 37005 esk Budjovice, Czech Republic
Laboratory of Analytical Biochemistry, Biology Centre of the ASCR, v.v.i., Branišovsk 31, 37005, esk Budjovice, Czech Republic
Department of Food Chemistry and Analysis, Institute of Chemical Technology, Technick 5, 16628 Prague 6, Czech Republic
Institute of Chemical Process Fundamentals of the ASCR, v.v.i., Rozvojov 135, 16502 Prague 6, Czech Republic


Two novel, structurally unusual cysteine derivatives were isolated from the bulbs of Allium stipitatum (Allium subg. Melanocrommyum) and shown to be S-(2-pyridyl)cysteine N-oxide and S-(2-pyridyl)glutathione N-oxide. The former compound is the first example of a naturally occurring alliinase substrate that contains an N-oxide functionality instead of the S-oxide group. In addition, S-methylcysteine S-oxide (methin) and S-(methylthiomethyl)cysteine 4-oxide (marasmin) were found in the bulbs. Presented data suggest that the previously reported identification of S-(2-pyridyl)cysteine S-oxide was most likely erroneous. The alliinase-mediated formation of pyridyl-containing compounds following disruption of A. stipitatum bulbs was studied by a combination of HPLC-MS, HPLC-PDA, DART-MS, and NMR techniques. It was found that no pyridyl-containing thiosulfimates are present in homogenized bulbs in detectable quantities. Instead, various pyridine N-oxide derivatives are formed, including N-hydroxypyridine-2(1H)-thione (pyrithione), 2-(methylthio)pyridine N-oxide, 2-[(methylthio)methylthio]pyridine N-oxide, di(2-pyridyl) disulfide N-oxide, and di(2-pyridyl) disulfide N,N'-dioxide. This represents the first report of pyrithione formation as a natural product.
Allium discoloration: the precursor and formation of the red pigment in giant onion (Allium giganteum Regel) and some other subgenus Melanocrommyum species

Kucerová, P.; Kubec, R.; Simek, P.; Václavík, L.; Schraml, J.

Department of Applied Chemistry, University of South Bohemia, Braniovsk 31, 370 05 esk Budjovice, Czech Republic
Laboratory of Analytical Biochemistry, Biology Centre of the ASCR, v.v.i., Braniovsk 31, 370 05, esk Budjovice, Czech Republic
Department of Food Chemistry and Analysis, Institute of Chemical Technology, Technick 5, 166 28 Prague 6, Czech Republic
Institute of Chemical Process Fundamentals of the ASCR, v.v.i., Rozvojov 135, 165 02 Prague 6, Czech Republic


The precursor of the orange-red pigment formed upon wounding the bulbs of Allium giganteum (Allium subg. Melanocrommyum) was isolated and shown to be S-(2-pyrrolyl)cytisteine 5-oxide. In addition, two other pyrrolylsulfinyl derivatives were found in an extract from the bulbs, namely, 3-(2-pyrrolylsulfinyl)lactic acid and S-(3-pyrrolyl)cytisteine 5-oxide. Contrary to a previous report, the latter compound was shown not to serve as the precursor of the pigment, being in fact only an artifact formed during isolation. The formation of pyrrolyl-containing compounds following disruption of A. giganteum bulbs was studied by a combination of LC–MS, LC–NMR and DART-MS. It was found that S-(2-pyrrolyl)cytisteine 5-oxide is cleaved by a C–S lyase (alliinase) to yield 2-pyrrolesulfenic acid. Two molecules of the latter compound give rise to highly reactive S-(2-pyrrolyl) 2-pyrrolylthiosulfinate which in turn converts into red 2,2′-epidithio-3,3′-dipyrrole (dipyrrolo[2,3-d:2′,3′-e]-1,2-dithiin). Several other pyrrolyl-containing compounds were detected in A. giganteum for the first time, including S-methyl 2-pyrrolylthiosulfinate, S-(2-pyrrolyl) methanethiosulfinate, di(2-pyrrolyl) disulfide, and S-(2-pyrrolyl) 2-pyrrolylthiosulfonate. It can be concluded that the formation of the orange-red pigment in Allium subg. Melanocrommyum species, despite sharing several analogous features, is of a different nature than the pink discoloration of onion.

Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis

Hajslova, J.; Cajka, T.; Vaclavik, L.

Institute of Chemical Technology, Prague, Technicka 3, 16628 Prague 6, Czech Republic.


Direct analysis in real time (DART) is an ambient ionization technique undergoing rapid development. With minimal sample pre-treatment, ionization of analyte molecules outside the mass spectrometry (MS) instrument in the ordinary atmosphere is feasible. This ionization approach relies upon the fundamental principles of atmospheric pressure chemical ionization.

The current review highlights and critically assesses application of DART (and some related desorption/ionization techniques) coupled to various types of MS analyzers for both target and non-target analysis of complex food matrices. Based on existing studies, DART-MS is presented as a simple, high-throughput tool for:

* (i) qualitative confirmation of chemical identity;
* (ii) metabolomic fingerprinting/profiling; and,
* (iii) quantification of low-molecular-weight food components, including some trace organic contaminants.

With regard to regulatory requirements, we mention practical aspects of DART-MS use, as well as performance characteristics that can be attained.
Analysis of multiple mycotoxins in beer employing (ultra)-high resolution mass spectrometry

Zachariasova, M.; Cajka, T.; Godula, M.; Malachova, A.; Veprikova, Z.; Hajslova

Institute of Chemical Technology, Prague, Technicka 3, 16628 Prague 6, Czech Republic.
Thermo Fisher Scientific, Czech Republic, Slunecná 27, 100 00 Prague 10, Czech Republic

J. Rapid Communications in Mass Spectrometry 2010, 24, 3357-3367

The objective of the presented study was to develop and optimize a simple, high-throughput method for the control of 32 mycotoxins (Fusarium and Alternaria toxins, aflatoxins, ergot alkaloids, ochratoxins, and sterigmatocystin) in beer. Due to the broad range of their physicochemical properties, the sample preparation step was simplified as much as possible to avoid analyte losses. The addition of acetonitrile to beer samples enabled precipitation of abundant matrix components. The clean-up efficiency was controlled by ambient mass spectrometry employing a direct analysis in real time (DART) ion source. For determination of analytes, ultra-high-performance liquid chromatography hyphenated with high-resolution mass spectrometry utilizing an orbitrap (U-HPLC–orbitrapMS) or time-of-flight (TOFMS) technology was used. Because of significantly better detection capabilities of the orbitrap technology, the U-HPLC–orbitrapMS method was chosen as a determinative step and fully validated. To compensate matrix effects, matrix-matched calibration was employed. The lowest calibration levels for most of the target mycotoxins ranged from 1 to 8 µg L−1 beer and the recoveries of analytes were in range from 86 to 124%.

Identification of marker compounds in herbal drugs on TLC with DART-MS

Kim, H. J.; Jee, E. H.; Ahn, K. S.; Choi, H. S.; Jang, Y. P.

Division of Pharmacognosy, College of Pharmacy, Kyung Hee University, Seoul, 130-701 Korea


This study was conducted to provide a more versatile and specific information on Thin Layer Chromatographic (TLC) analysis of medicinal plants. TLC plates developed with the extract of herbal medicines were analyzed with direct analysis in real time (DART) ion source. Three well known herbal drugs were extracted and developed on a silica-coated TLC plate with the conditions pre-established in Korean Pharmacopoeia IX. The developed plate was placed between the DART ion source and TOF-MS analyzer to get real time mass spectra from the bands on the TLC plate directly. The marker coumarin compounds, decursin and decursinol were successfully identified from the TLC plate developed with Angelicae gigantis radix, along with alkaloid compounds of rutaecarpine and evodiamine from Evodiae fructus, and lignan molecules of gomisin A, N, and schisandrins from Schisandraceae fructus. This hyphenation system of TLC and DART-MS could provide unique and specific information on the major constituents of crude plant drug on TLC through uncovering high resolution mass number of each band on the TLC plate directly in real time.
Analysis of multiple mycotoxins in cereals under ambient conditions using direct analysis in real time (DART) ionization coupled to high resolution mass spectrometry

Lukas Vaclavik, Milena Zachariasova, Vojtech Hrbek and Jana Hajslova

Institute of Chemical Technology Prague, Department of Food Chemistry and Analysis, Technicka 5, 16628 Prague 6, Czech Republic
doi:10.1016/j.talanta.2010.08.029
http://dx.doi.org/10.1016/j.talanta.2010.08.029

Direct analysis in real time (DART) ionization coupled to an (ultra)high resolution mass spectrometer based on orbitrap technology (orbitrapMS) was used for rapid quantitative analysis of multiple mycotoxins isolated from wheat and maize by modified QuEChERS procedure. After initial evaluation of ionization efficiencies for major groups of mycotoxins achievable with DART technology, sample preparation procedure and instrument parameter settings were optimized to obtain sensitive and accurate determination of most intensively ionizing toxins (deoxynivalenol, nivalenol, zearalenon, acetyldeoxynivalenol, deepoxy-deoxynivalenol, fusarenon-X, altenuene, alternariol, alternariomethylether, diacetoxyisocirpenol, sterigmatocystin). The lowest calibration levels (LCLs) estimated for the respective analytes ranged from 50 to 150 µg kg⁻¹. Quantitative analysis was performed either with the use of matrix-matched standards or by employing commercially available 13C-labeled internal standards (available for deoxynivalenol, nivalenol and zearalenon). Good recoveries (100-108%) and repeatabilities (RSD 5.4-6.9%) were obtained at spiking level 500 µg kg⁻¹ with isotope dilution technique. Based on matrix-matched calibration, recoveries and repeatabilities were in the range 84-118% and 7.9-12.0% (RSD), respectively. The trueness of data obtained for deoxynivalenol and zearalenon in wheat/maize by DART–orbitrapMS was demonstrated by analysis of certified reference materials (CRMs). Good agreement of these results with data generated by validated ultra high pressure liquid chromatography–time-of-flight mass spectrometry method was documented.

Selective ionization of melamine in powdered milk by using argon direct analysis in real time (DART) mass spectrometry.

Dane AJ, Cody RB.

JEOL USA Inc., 11 Dearborn Rd., Peabody, MA 01960, USA.


5-Hydroxymethylfurfural (5-HMF) is a compound with the elemental composition C(6)H(6)O(3) that is present in powdered milk. Protonated 5-HMF (calculated m/z 127.0395) has the same nominal m/z as protonated melamine (calculated m/z 127.0732) and can interfere with direct analysis of melamine in powdered milk. Tandem mass spectrometry and high-resolution mass spectrometry have been previously used to distinguish melamine from 5-HMF. An alternative approach is presented here that uses the direct analysis in real time (DART) ion source operated with argon gas in combination with acetylacetone and pyridine reagent gases to selectively ionize melamine and eliminate the interference from 5-HMF. High-resolution/accurate mass data were used to verify the elimination of the 5-HMF interference and confirm the melamine elemental composition. With further refinement, this technique could lead to a rapid analysis method for screening large numbers of samples.
Rapid identification of additives in poly(vinyl chloride) lid gaskets by direct analysis in real time ionisation and single-quadrupole mass spectrometry

Thorsten Rothenbacher, Wolfgang Schwack
Institut für Lebensmittelchemie, Universität Hohenheim, Garbenstrasse 28, 70599 Stuttgart, Germany

Gaskets for lids of glass jars usually consist of poly(vinyl chloride) (PVC) containing plasticisers and additional additives, which may migrate into packed foodstuffs. To conform to legal regulations, any such migration has to be determined analytically, which is a big challenge due to the huge chemical variety of additives in use. Therefore, a rapid screening method by means of direct analysis in real time mass spectrometry (DART-MS), using a single-quadrupole mass spectrometer, was developed. On introducing a plastisol sample into the DART interface, protonated molecules and ammonium adducts were obtained as the typical ionisation products of any additives present, and cleavages of ester bonds as typical fragmentation processes. Generally, additives present in the 1% range could be directly and easily identified if ion suppressive effects deriving from specific molecules did not occur. These effects could be avoided by analysing toluene extracts of plastisol samples, and this also improved the sensivity. Using this method, it was possible to identify phthalates, fatty acid amides, tributyl O-acetylcitrate, dibutyl sebacate, bis(2-ethylhexyl) adipate, 1,2-disononyl 1,2-cyclohexanedicarboxylate, and even more complex additives like acetylated mono- and diacylglycerides, epoxidised soybean oil, and polyadipates, with a limit of detection of ≤1% in PVC plastisols. Only in the case of epoxidised linseed oil were levels of ≥5% required for identification. The detection of azodicarbonamide, used as a foaming agent within the manufacturing process, was possible in principle, but was not highly reproducible due to the very low concentrations in plastisols.

Release kinetics of actives from chewing gums into saliva monitored by direct analysis in real time mass spectrometry.

Jeckelmann N, Haefliger OP
Firmenich SA, Corporate R&D Division, P.O. Box 239, 1211 Geneva 8, Switzerland.

Direct analysis in real time mass spectrometry (DART-MS) was used to monitor the release kinetics of a taste-refreshing compound from chewing gums into the saliva of subjects. A new DART-MS sample probe was designed which was about four times more sensitive than the current benchmark probe. This decreased the impact of the dilution of the saliva samples that was required to minimize ion suppression effects and make quantitative analyses without an internal standard possible. The new probe was also about three times more reproducible, which allowed quantitative measurements to be conducted manually without requiring the enhanced precision provided by an automatic sample positioner. The accuracy of analyses performed by DART-MS was verified by comparing the results obtained from saliva samples analyzed both by DART-MS and by a more classical liquid chromatography/mass spectrometry (LC/MS) method. This investigation showed good agreement between the two techniques. DART-MS could then be used to objectively demonstrate the efficiency of a granular carbohydrate-based delivery system to boost for a few minutes the release of a lipophilic flavor raw material with a high octanol/water partition coefficient, cyclohexanecarboxamide, N-ethyl-5-methyl-2-(1-methylethyl) (WS-3), from chewing gum into saliva.
Applications of direct analysis in real time-mass spectrometry (DART-MS) in Allium chemistry. (Z)-butanethial S-oxide and 1-butenyl thiosulfimates and their S-(E)-1-butenylcysteine S-oxide precursor from Allium siculum.

Kubec R, Cody RB, Dane AJ, Musah RA, Schraml J, Vattekkatte A, Block E

Department of Applied Chemistry, University of South Bohemia, Branisovska 31, 370 05 Ceske Budejovice, Czech Republic.


Lachrymatory (Z)-butanethial S-oxide along with several 1-butenyl thiosulfimates was detected by DART mass spectrometry upon cutting Allium siculum, a popular ornamental Allium species used in some cultures as a spice. (Z)-Butanethial S-oxide isolated from the plant was shown to be identical to a synthetic sample. Its likely precursor, (R(S),R(C),E)-S-(1-butenyl)cysteine S-oxide (homoisoalliin), was isolated from homogenates of A. siculum, and a closely related species Allium tripedale, and fully characterized. Through use of LC-MS, a series of related gamma-glutamyl derivatives were tentatively identified in A. siculum and A. tripedale homogenates, including gamma-glutamyl-(E)-S-(1-butenyl)cysteine and its S-oxide, gamma-glutamyl-S-butylcysteine and its S-oxide, and gamma-glutamyl-S-methylcysteine and its S-oxide. Because compounds containing the 1-butenyl group have not been previously identified in genus Allium species, this work extends the range of known Allium sulfur compounds. The general applicability of DART mass spectrometry in identifying naturally occurring, thermally fragile thial S-oxides and thiosulfimates is illustrated with onion, Allium cepa, as well as a plant from a different genus, Petiveria alliacea.

Profiling of Piper betle Linn. cultivars by direct analysis in real time mass spectrometric technique

Bajpai, V., Sharma, D., Kumar, B. and Madhusudanan, K. P.

Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow-226001, India.

Biomedical Chromatography, doi: 10.1002/bmc.1437

Piper betle Linn. is a traditional plant associated with the Asian and southeast Asian cultures. Its use is also recorded in folk medicines in these regions. Several of its medicinal properties have recently been proven. Phytochemical analysis showed the presence of mainly terpenes and phenols in betel leaves. These constituents vary in the different cultivars of Piper betle. In this paper we have attempted to profile eight locally available betel cultivars using the recently developed mass spectral ionization technique of direct analysis in real time (DART). Principal component analysis has also been employed to analyze the DART MS data of these betel cultivars. The results show that the cultivars of Piper betle could be differentiated using DART MS data.
Allium chemistry: Use of new instrumental techniques to “see” reactive organosulfur species formed upon crushing garlic and onion

Eric Block, Robert B. Cody, A. John Dane, Robert Sheridan, Abith Vattekkatte and Kai Wang

Department of Chemistry, University at Albany, SUNY, Albany, NY 12222, USA
JEOL USA, Inc., 11 Dearborn Road, Peabody, MA 01960, USA
New York State Department of Agriculture and Markets, Food Laboratory Division, Albany, NY 12235, USA


Three different instrumental methods have been used to examine the organosulfur chemistry of intact and cut garlic and onions: X-ray fluorescence spectroscopic imaging (XFS), direct analysis in real time (DART) mass spectrometry, and ultra-performance liquid chromatography-(Ag+)-coordination ion spray mass spectrometry (UPLC–(Ag+)CIS–MS). The first technique has been used to map the location of different chemical forms of sulfur in intact and damaged onion cells, the second technique, to identify the reactive, volatile sulfur compounds formed on cutting the plants, and the third technique, to identify members of families of polysulfides found in the distilled oil of garlic.

Ambient mass spectrometry employing direct analysis in real time (DART) ion source for olive oil quality and authenticity assessment.

Vaclavik L, Cajka T, Hrbek V, Hajslova J.

Institute of Chemical Technology Prague, Faculty of Food and Biochemical Technology, Department of Food Chemistry and Analysis, Technicka 5, 166 28 Prague 6, Czech Republic.


A novel approach for the authentication of olive oil samples representing different quality grades has been developed. A new type of ion source, direct analysis in real time (DART), coupled to a high-resolution time-of-flight mass spectrometer (TOFMS) was employed for the comprehensive profiling of triacylglycerols (TAGs) and/or polar compounds extracted with a methanol-water mixture. The main parameters influencing the ionization efficiency of TAGs were the type of sample solvent, degree of sample dilution, ion beam temperature, and presence of a dopant (ammonia vapors). The ionization yield of polar compounds depended mainly on a content of water in the extract and ion beam temperature. Using DART-TOFMS, not only differentiation among extra virgin olive oil (EVOO), olive pomace oil (OPO) and olive oil (OO) could be easily achieved, but also EVOO adulteration with commonly used adulterant, hazelnut oil (HO), was feasible. Based on the linear discriminant analysis (LDA), the introduced method allowed detection of HO addition of 6 and 15% (v/v) when assessing DART-TOFMS mass profiles of polar compounds and TAGs, respectively.
Assessing direct analysis in real time-mass spectrometry (DART-MS) for the rapid identification of additives in food packaging

Ackerman, L.K.; Noonan, G.O.; Begley, T.H.

US Food and Drug Administration (USFDA), Center for Food Safety and Applied Nutrition, College Park, MD 20740, USA


The ambient ionization technique direct analysis in real time (DART) was characterized and evaluated for the screening of food packaging for the presence of packaging additives using a benchtop mass spectrometer (MS). Approximate optimum conditions were determined for 13 common food-packaging additives, including plasticizers, anti-oxidants, colorants, grease-proofers, and ultraviolet light stabilizers. Method sensitivity and linearity were evaluated using solutions and characterized polymer samples. Additionally, the response of a model additive (di-ethyl-hexyl-phthalate) was examined across a range of sample positions, DART, and MS conditions (temperature, voltage and helium flow). Under optimal conditions, molecular ion (M+H)+ was the major ion for most additives. Additive responses were highly sensitive to sample and DART source orientation, as well as to DART flow rates, temperatures, and MS inlet voltages, respectively. DART-MS response was neither consistently linear nor quantitative in this setting, and sensitivity varied by additive. All additives studied were rapidly identified in multiple food-packaging materials by DART-MS/MS, suggesting this technique can be used to screen food packaging rapidly. However, method sensitivity and quantitation requires further study and improvement.

Direct analysis of curcumin in turmeric by DART-MS.

Kim HJ, Jang YP.

Kyung Hee East-West Pharmaceutical Research Institute, College of Pharmacy, Kyung Hee University, Seoul, Korea.


The new ion source technique, direct analysis in real time (DART) atmospheric pressure ionisation, allows high resolution mass measurements of gas, liquid and solid samples. As DART-MS produces [M + H]+ molecular ions of most compounds, relatively simple and clear mass spectra are obtained even of multi-component samples. In order to take advantage of the capacity of DART-MS for the real time analysis of individual compounds in natural raw materials, a pilot study was performed using the well-known antioxidant botanical drug, turmeric.

OBJECTIVE: To establish the analysis methods of curcumin and its derivatives from various types of samples with DART-MS and compare the efficiency of the method with traditional HPLC method.

RESULTS: Different curcuminoids were successfully detected directly from the raw particles of Curcuma longa. When a turmeric extract was separated on a TLC plate, each band produced molecular ion peaks corresponding to curcumin, demethoxycurcumin and bisdemethoxycurcumin. Molecular ions of curcuminoids in turmeric-containing beverages and curry powder were also efficiently detected. In addition to high efficiency of qualitative analysis, the evaluation of its linearity showed that DART-MS can be applied for semi-quantitative determinations of curcumin over a large range (5-100 microg/mL).

CONCLUSION: A simple chemical profiling and semi-quantitative method for natural products using DART-MS might be applied to diverse field related quality control of medicinal plants or food ingredients.
Temperature-dependent release of volatile organic compounds of eucalypts by direct analysis in real time (DART) mass spectrometry.

Maleknia SD, Vail TM, Cody RB, Sparkman DO, Bell TL, Adams MA.

School of Biological, Earth & Environmental Sciences, University of New South Wales, Sydney, NSW, Australia.


A method is described for the rapid identification of biogenic, volatile organic compounds (VOCs) emitted by plants, including the analysis of the temperature dependence of those emissions. Direct analysis in real time (DART) enabled ionization of VOCs from stem and leaf of several eucalyptus species including E. cinerea, E. citriodora, E. nichollii and E. sideroxylon. Plant tissues were placed directly in the gap between the DART ionization source skimmer and the capillary inlet of the time-of-flight (TOF) mass spectrometer. Temperature-dependent emission of VOCs was achieved by adjusting the temperature of the helium gas into the DART ionization source at 50, 100, 200 and 300 degrees C, which enabled direct evaporation of compounds, up to the onset of pyrolysis of plant fibres (i.e. cellulose and lignin). Accurate mass measurements facilitated by TOF mass spectrometry provided elemental compositions for the VOCs. A wide range of compounds was detected from simple organic compounds (i.e. methanol and acetone) to a series of monoterpenes (i.e. pinene, camphene, cymene, eucalyptol) common to many plant species, as well as several less abundant sesquiterpenes and flavonoids (i.e. naringenin, spathulenol, eucalyptin) with antioxidant and antimicrobial properties. The leaf and stem tissues for all four eucalypt species showed similar compounds. The relative abundances of methanol and ethanol were greater in stem wood than in leaf tissue suggesting that DART could be used to investigate the tissue-specific transport and emissions of VOCs.

Pro-inflammatory enzymes, cyclooxygenase 1, cyclooxygenase 2, and 5-lipooxygenase, inhibited by stabilized rice bran extracts.

Roschek B Jr, Fink RC, Li D, McMichael M, Tower CM, Smith RD, Alberte RS.

HerbalScience Group LLC, Naples, Florida 34110, USA.


Rice bran, the outer bran and germ of the kernel and a by-product of rice milling, is rich in phytonutrients but has been underutilized because of lipid content instability. New methods for the processing of rice bran have yielded a stabilized form that is increasingly used in foods and dietary supplements. Recent studies have documented a role for stabilized rice bran (SRB) in treating diabetes and arthritis, although little is known of the bioactive compounds that impart these health benefits. Here we characterize the chemical composition of three extracts of SRB and identify the functional bioactives contributing to the inhibitory properties against three key pro-inflammatory enzymes (cyclooxygenase [COX] 1, COX2, and 5-lipooxygenase [5-LOX]) that control the inflammatory cascade involved in impaired joint health, pain, and arthritis. One extract (SRB-AI) demonstrated significant COX1 and COX2 inhibitory activities with 50% inhibitory concentration (IC(50)) values for COX1 and COX2 of 305 and 29 microg/mL, respectively, but no 5-LOX inhibition. The second extract (SRB-AII) inhibited COX1, COX2, and 5-LOX with IC(50) values of 310, 19, and 396 microg/mL, respectively. The third extract (SRB-AIII), a blend of SRB-AI and SRB-AII, inhibited COX1, COX2, and 5-LOX with respective IC(50) values of 48, 11, and 197 microg/mL. Analysis of the extracts by direct analysis in real time time of flight-mass spectrometry revealed that SRB-AI, SRB-AII, and SRB-AIII contain over 620, 770, and 810 compounds, respectively. Of these, 17 were identified as key bioactives for COX and/or LOX inhibition. These SRB extracts have applications for functional foods and dietary supplements for control of inflammation and joint health.
Elderberry flavonoids bind to and prevent H1N1 infection in vitro.

Roschek B Jr, Fink RC, McMichael MD, Li D, Alberte RS.

HerbalScience Group LLC, 1004 Collier Center Way, Suite 200, Naples, FL 34110, USA.


A ionization technique in mass spectrometry called Direct Analysis in Real Time Mass Spectrometry (DART TOF-MS) coupled with a Direct Binding Assay was used to identify and characterize anti-viral components of an elderberry fruit (Sambucus nigra L.) extract without either derivatization or separation by standard chromatographic techniques. The elderberry extract inhibited Human Influenza A (H1N1) infection in vitro with an IC(50) value of 252 +/- 34 microg/mL. The Direct Binding Assay established that flavonoids from the elderberry extract bind to H1N1 virions and, when bound, block the ability of the viruses to infect host cells. Two compounds were identified, 5,7,3',4'-tetra-O-methylquercetin (1) and 5,7-dihydroxy-4-oxo-2-(3,4,5-trihydroxyphenyl)chroman-3-yl-3,4,5-trihydroxycyclohexanecarboxylate (2), as H1N1-bound chemical species. Compound 1 and dihydromyricetin (3), the corresponding 3-hydroxyflavonone of 2, were synthesized and shown to inhibit H1N1 infection in vitro by binding to H1N1 virions, blocking host cell entry and/or recognition. Compound 1 gave an IC(50) of 0.13 microg/mL (0.36 microM) for H1N1 infection inhibition, while dihydromyricetin (3) achieved an IC(50) of 2.8 microg/mL (8.7 microM). The H1N1 inhibition activities of the elderberry flavonoids compare favorably to the known anti-influenza activities of Oseltamivir (Tamiflu; 0.32 microM) and Amantadine (27 microM).

Identification of active ingredients in dietary supplements using non-destructive mass spectrometry and liquid chromatography–mass spectrometry

Kanju Saka@, Kiyotaka Konumab, Shigehiro Asaic, Kana Unumaa, Makoto Nakajimaa, Ken-ichi Yoshidaa

Department of Forensic Medicine, Graduate School of Medicine, University of Tokyo, Tokyo 113-0033, Japan.


A mid-forties woman purchased seven different dietary supplements from Thailand on the internet and subsequently died after taking these supplements. Since there were no ingredient labels on the supplements, we identified the active ingredients using direct analysis in real time–mass spectrometry (DART–MS), direct exposure probe–MS (DEP–MS), and liquid chromatography–MS (LC–MS). DART–MS gives exact molecular weights and DEP–MS shows the fragmentation of a molecule by electron ionization. Analyses using these two instruments are rapid and do not require extraction of the sample. The compounds predicted by DART–MS and DEP–MS were confirmed by LC–MS and the active ingredients of the seven dietary supplements were identified.
Control of Strobilurin Fungicides in Wheat Using Direct Analysis in Real Time Accurate Time-of-Flight and Desorption Electrospray Ionization Linear Ion Trap Mass Spectrometry


Department of Food Chemistry and Analysis, Institute of Chemical Technology Prague, Technick 5, 6 Prague 16628, Czech Republic, RIKILT Institute of Food Safety, P.O. Box 230, 6700 AE Wageningen, The Netherlands, Central Science Laboratory, Sand Hutton, York, U.K. YO41 1LZ Wageningen University, Laboratory of Organic Chemistry, Dreijenplein 8, 6703 HB Wageningen, The Netherlands


Ambient mass spectrometry has been used for the analysis of strobilurin residues in wheat. The use of this novel, challenging technique, employing a direct analysis in a real time (DART) ion-source coupled with a time-of-flight mass spectrometer (TOF MS) and a desorption electrospray ionization (DESI) source coupled with a linear ion trap tandem MS (LIT MSn), permitted a direct screen of the occurrence of target fungicides in treated grains in less than 1 min. For quantification purpose by DART-TOF MS, an ethyl acetate extract had to be prepared. With the use of a prochloraz as an internal standard, the performance characteristics obtained by repeated analyses of extract, spiked at 50 µg kg−1 with six strobilurins (azoxystrobin, picoxystrobin, dimoxystrobin, kresoxim-methyl, pyraclostrobin, and trifloxystrobin), were in the following range: recoveries 78–92%, repeatability (RSD) 8–15%, linearity (R2) 0.9900–0.9978. The analysis of wheat with incurred strobilurin residues demonstrated good trueness of data generated by the DART-TOF MS method; the results were in a good agreement with those obtained by the conventional approach, i.e., by the QuEChERS sample handling procedure followed by identification/quantification employing high-performance liquid chromatography coupled with tandem mass spectrometry (LC–MS/MS). Tandem mass spectrometry using DESI-LIT MSn provided a sufficient number of product ions for confirmation of the identity of azoxystrobin and pyraclostrobin in incurred wheat samples.

Direct analysis in real time–time-of-flight mass spectrometry: Analysis of pesticide residues and environmental contaminants

Lukáš Václavík, Jakub Schůrek, Tomáš Čajka and Jana Hajšlová

Department of Food Chemistry and Analysis, Institute of Chemical Technology Prague, Technicka 5, 166 28 Prague 6 Dejvice, Czech Republic,

Chemie Listy, 2008, 102(15), s324–s327.

DART–TOFMS technique can be used for determination of strobilurin fungicides in milled wheat grain extracts obtained by simple extraction procedure without time-consuming chromatographic separation. This method withstands the regulation demands of the European Union for the control of pesticide residues; moreover, simplified workflow enables examination of many samples within a short time period. Qualitative analysis of solid samples without any sample preparation is a challenging application of this novel technique. DAR T–TOFMS was shown to be a useful tool enabling rapid examination of plant surface and detection of pesticide used for flower treatment. Preliminary results indicate the potential to introduce new concepts into rapid screening of BFRs by employing DART T–TOFMS. In addition, the information provided by both negative and positive mass spectra should be exploited with the aim to detect the presence of other contaminants.
Analysis of hairy root culture of Rauvolfia serpentina using direct analysis in real time mass spectrometric technique.

Madhusudanan KP, Banerjee S, Khanuja SP, Chattopadhyay SK.

Sophisticated Analytical Instrument Facility, Central Drug Research Institute, Lucknow-226015, India.


The applicability of a new mass spectrometric technique, DART (direct analysis in real time) has been studied in the analysis of the hairy root culture of Rauvolfia serpentina. The intact hairy roots were analyzed by holding them in the gap between the DART source and the mass spectrometer for measurements. Two nitrogen-containing compounds, vomilenine and reserpine, were characterized from the analysis of the hairy roots almost instantaneously. The confirmation of the structures of the identified compounds was made through their accurate molecular formula determinations. This is the first report of the application of DART technique for the characterization of compounds that are expressed in the hairy root cultures of Rauvolfia serpentina. Moreover, this also constitutes the first report of expression of reserpine in the hairy root culture of Rauvolfia serpentina.

GC–TOF-MS and DART–TOF-MS: Challenges in the Analysis of Soft Drinks

Tomas Cajka, Lukas Vaclavik, Katerina Riddellova, Jana Hajslova

Institute of Chemical Technology, Faculty of Food and Biochemical Technology, Department of Food Chemistry and Analysis, Prague, Czech Republic.

LCGC Europe Volume 21, Issue 5, 2008

The first case study involving the application of the head-space SPME–GC–TOF-MS combined with advanced data processing is a powerful tool to detect, identify, and automate the reporting trace peak of sensorically active taint compound present in soft drinks that would be "invisible" under the conditions commonly used, such as using GC coupled to conventional quadrupole or ion trap mass analysers. The second case study demonstrated the unique potential of a new ion source: direct analysis in real time (DART) coupled to a high-resolution time-of-flight-mass spectrometer (TOF-MS). The presence of a whole array of drink components could be detected and identified within a couple of seconds without any sample preparation. The distinguishing factors between two types of otherwise equally tasting soft drinks could be obtained on the basis of the proof of additives used. Further research aimed at obtaining performance characteristics such as limit of detection (LOD) and repeatability of measurement is currently being investigated.
Expression of tropane alkaloids in the hairy root culture of Atropa acuminata substantiated by DART mass spectrometric technique.

Banerjee S, Madhusudanan KP, Chattopadhyay SK, Rahman LU, Kahanja SP.

Central Institute of Medicinal and Aromatic Plants, PO CIMAP, Lucknow, India.


Agrobacterium rhizogenes-mediated 'hairy root' cultures were established in Atropa acuminata. The chemical profiling of the hairy roots was carried out by a new mass spectrometric technique, direct analysis in real time (DART). The intact hairy roots were directly analyzed by holding them in the gap between the DART ion source and mass spectrometer. Two alkaloids, atropine and scopolamine, were characterized. The structural confirmation of the two alkaloids was made through their accurate molecular formula determinations. This is the first report of establishing hairy roots in A. acuminata as well as application of the DART technique for the chemical profiling of its hairy roots.

Pharmacokinetics of Cyanidin and Anti-Influenza Phytonutrients in an Elder Berry Extract Determined by LC-MS and DART TOF-MS

Bill Roschek Jr., Randall S. Alberte*

HerbalScience Group LLC., Naples FL 34110, USA

Online J Pharmacol Pharmacokin, Volume 4: 1-17, 2008

Roschek B Jr, Alberte RS, Pharmacokinetics of Cyanidin and Anti-Influenza Phytonutrients in an Elder Berry Extract Determined by LC-MS and DART TOF-MS Online J Pharmacokinetics, 4: 1-17, 2008 Pharmacokinetic analyses were conducted on flavonoid phytonutrients in a Standardized Elder Berry Extract (SEBX) to determine bioavailability and uptake kinetics, and to compare LC-MS and DART TOF-MS for pharmacokinetic analyses. In the first study, serum and urine levels of Cyanidin from an SEBX lozenge were monitored by LC-MS in 6 individuals. In the second study, DART TOF-MS was used to compare the serum pharmacokinetics and bioavailability of Cyanidin and other flavonoids in SEBX when delivered as a slow-dissolve lozenge and as a drink from a single individual. When the SEBX lozenge was consumed, serum concentrations of Cyanidin were between 3.1 (LC-MS) and 5.4 nmol L-1 (DART TOF-MS), equivalent to 2.7 and 4.7% bioavailability (BA), respectively. Averionol (methylated flavonoid) reached a Cmax of 23 nmol L-1 (10.5% BA), while Tristenonol (esterified flavonoid) and Istrocyanidin (A-type proanthocyanidin) reached Cmax values of 3.9 nmol L-1 (8.6% BA) and 7.5 nmol L-1 (19.7% BA), respectively. When the SEBX was consumed as a drink, the bioavailability of Cyanidin decreased 20-fold (0.2% BA), while Averionol and Istrocyanidin decreased 2-fold (4.6 and 10.8% BA, respectively) compared to the lozenge ingestion, indicating primary uptake in the oral cavity. The bioavailability of Tristenonol increased by ca. 2-fold (18.8% BA) when the SEBX drink was consumed compared to the lozenge indicating the small intestine as the primary uptake site.
Your customers trust your brand

Screen more often to protect it
Create your rapid sampling, low cost protection plan with DART-MS

IonSense.com

Identify Problems in Seconds

Detect Adulterants and Counterfeits

Screen for Pesticide Residues

Authenticate Finished Products and Raw Materials

- Dietary Supplements
- Wines and Spirits
- Food Oils
- Botanicals