敞开式离子化质谱在食品安全快速筛查中的应用

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摘　要: 敞开式离子化质谱(ambient mass spectrometry, AMS)是一种能在大气压环境中对样品进行解吸并离子化, 从而获得样品表面信息的新型质谱技术。由于其具有快速、原位、实时分析等优势, 近年来被广泛应用于食品安全快速筛查领域。本文从霉菌毒素类物质的检测, 食品中非法添加物的快速筛查, 食品本身有毒有害物质的鉴定, 食品质量监控, 食品组成成分分析和监测食品中的化学反应六个方面, 综述了以实时直接分析(direct analysis in real time, DART)离子化技术为主的 AMS 技术在食品安全分析领域的应用。

关键词: 敞开式离子化质谱; 实时直接分析; 食品安全; 快速筛查

Applications of ambient mass spectrometry for rapid screening in food safety

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ABSTRACT: Ambient mass spectrometry(AMS) is a kind of new techniquesthat performs under atmospheric pressure environment, allowing the analysis of sample surfaces. Due to the advantages such as high throughput, real time analysis in situ, no solvent waste, it is widely applied in the rapid screening of food safety. This review presented the applications of ambient mass spectrometry(especially direct analysis in real time) for rapid screening in food safety,including the analysis of mycotoxins, illegal additives, toxic and harmful substances, quality control, food components, and the chemical reactions in food.

KEY WORDS:ambient mass spectrometry; direct analysis in real time; food safety; rapid screening

1　引　言

敞开式离子化质谱(ambient mass spectrometry, AMS)是一种能在大气压环境中对样品进行解吸并离子化, 从而获得样品表面信息的新型质谱技术。这种质谱技术的最大优点是无需或只需简单的样品前处理过程, 从而大大缩短分析时间, 实现了高通量分析。由于解吸方式和离子化机理的不同, 目前已经报道了超过 30 种 AMS 技术, 例如解吸电喷雾离子源(desorption electrospray ionization, DESI)[1]、实时直接分析离子源(direct analysis in real time, DART)[2]、介质阻挡放电离子源(dielectric barrier discharge ionization, DBDI)[3]、大气压解吸光电离源(desorption atmospheric pressure photoionization, DAPPI)[4]等。目前, AMS 技术已被广泛应用于食品安全筛查[5]、爆炸物监测[6]、司法鉴定[7]、化学反应监控[8]、生物分子及代谢物表征[9]等领域。由于仪器的商品化, DART 和 DESI 的应用尤其广泛。本文重点介绍以 DART 技术为主的 AMS 技术在食品安全快速筛查中的应用(见图 1)。

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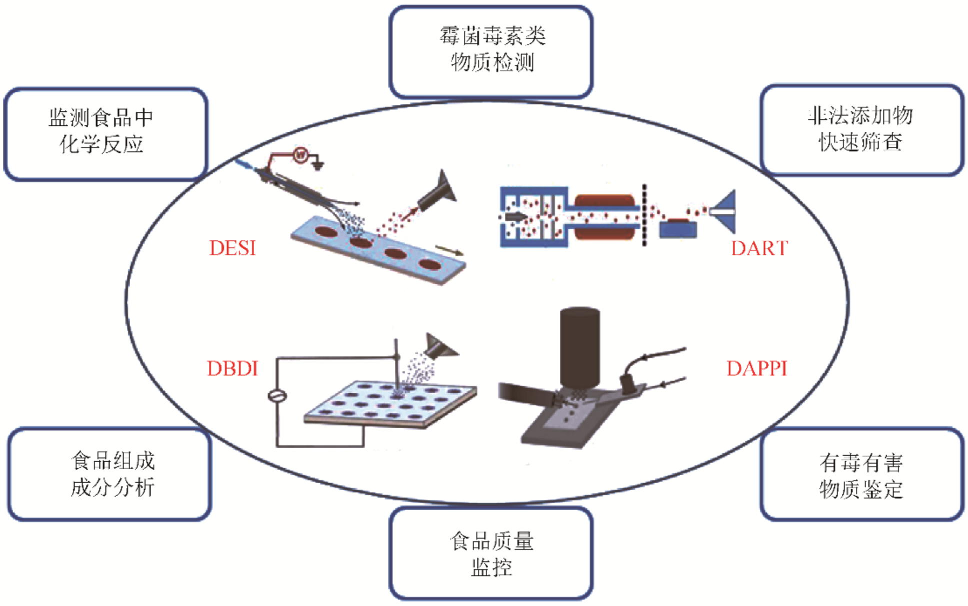

图 1AMS 技术在食品安全快速筛查中的应用
Fig.1Applications of ambient mass spectrometry for rapid screening in food safety

2 霉菌毒素类物质的检测

黄曲霉素是霉菌毒素中毒性最大的一类毒素，存在于土壤和各类坚果中，特别容易污染花生、玉米等粮油食品，它的危害性在于对人及动物肝脏组织有破坏作用，严重时可导致肝癌甚至死亡。Busman 等[10]利用 DART 离子源结合高分辨质谱(mass spectrometry, MS)对玉米中的黄曲霉毒素 AFB_1 进行快速筛查。利用 ^{13}C 标记的内标物可实现对 AFB_1 的定量分析，在 4~1000 μg/kg 范围内呈现线性响应。随后，他们又用同样的方法对牛奶中的黄曲霉毒素 AFM_1 进行定性定量分析[11]。AFM_1 是 AFB_1 在动物体内的代谢产物，AFB_1 在奶牛体内会有部分转化为 AFM_1 并分泌到牛奶中。该方法的定量限为 0.1μg/kg，低于美国联邦政府规定的人类消费的牛奶中 AFM_1 含量不超过 0.5μg/kg 的标准。此外，还有人利用 DART 离子源结合轨道阱高分辨 MS 对小麦玉米中玉米赤霉烯酮等毒素[12]和八角茴香中莽草毒素[13]进行了鉴定。除了 DART 之外，DESI 离子源结合离子阱 MS 也可实现对玉米粒中伏马菌素 B_1 的分析[14]。

3 食品药品中非法添加物的快速筛查

食品当中的非法添加严重危害人们的健康。2008 年，一些违法商家将化工用原料三聚氰胺(melamine, MEL)添加到婴幼儿奶粉中，导致食用该奶粉的很多婴儿被查出肾结石。而在 2012 年 9 月，新西兰恒天然集团被查出奶粉中含有二聚氰胺(dicyandiamine, DCD)物质。Vaclavik 等[15]利用 DART 离子源结合四极杆飞行时间质谱(quadrupole time-of-flight mass spectrometry, Q-TOF MS)对奶粉及炼乳、乳酪等奶制品中的 MEL 和三聚氰酸进行筛查，检出限分别为 170 μg/kg 和 450 μg/kg，远低于美国食品与药物管理局(US Food and Drug Administration, FDA)以及欧盟规定的 2.5 mg/kg 的安全限值。同样利用 DART 离子源结合 Q-TOF MS/MS，Zhang 等[16]对奶粉中的 DCD 进行定性和定量分析，提供了一种快速检出奶粉中 DCD 的有效方法。Yang 等[17]则利用大气压解吸化学电离质谱(DAPCI-MS)对牛奶中的 MEL 进行检测。质子化 MEL 的碎片离子(m/z=85)的强度与牛奶中 MEL 含量正相关，线性范围达 5 个数量级，检出限则低至 3.4×10^{-15} g/mm^2，并且每个样品分析仅需几秒钟，大大缩短了分析时间。Liu 课题组[18]用 DART 结合 Q-TOF MS/MS 对市售辣椒粉中的 4 种苏丹染料进行了快速筛查。对 DART-MS 的工作气类型、温度、DART 孔口与质谱入口距离和样品移动速度进行系统优化，通过简单的己烷萃取后，直接利用熔融玻璃管进样器(商品名 Dip it)蘸取己烷萃取液进行分析。4 种染料在甲醇中的检出限为 80~100 ng/mL 不等。该方法简便快速(15 min)并拥有良好的线性(r^2＞0.99)、重现性(n=6，RSD＜15%)和回收率(88%~116%)，适用于食品中苏丹染料的快速筛查。同样针对苏丹染料，Chen 等[19]和 Taverna 等[20]分别利用 DESI-MS^2 和纸喷雾 MS 进行分析，检出限分别为 0.01~1.0 pg/mm^2 和 1 μg/g。在药品检测方面，Liu 课题组[21]利用 DART-MS 对中药降糖类保健药中非法添加的西药进行了快速筛查。通过用甲醇:水(1:1, V:V)对中药保健品进行萃取，之后直接进行 DART 分析，可实现对 7 种非法添加成分(格列齐特、格列甲嗪、二甲双胍、那格列奈、罗格列酮、格列本脲和格列喹酮)

的快速检出(见图 2)。整个分析过程在 10 min 之内完成, 检出限达到 2~400 μg/g(格列甲嗪检测限为 3 mg/g), 完全满足市场上对降糖类药物进行筛查的需求。

4　食品中有毒有害物质的鉴定

水果在种植过程中, 可能在果皮上残留一些杀菌剂, 为了实现对水果果皮上残留的有毒有害物质进行筛查, Farre 等[22]利用 DART 离子源结合高分辨离子阱 MS 在正离子模式下对苹果、梨、柠檬果皮上残留的杀菌剂、氧化剂及糖类物质进行定性定量分析。抑霉唑杀菌剂的检出限低至 300 μg/kg, 远低于规定的最高残留限(2 mg/kg), 并可在 1~2500 ng 范围内实现定量分析。该研究人员将 DART-MS 方法与超高效液相色谱结合离子阱 MS 分析方法相比, 两者结果有较好的一致性, 说明 DART-MS 是一种快速且可准确定量的分析方法。同样是检测杀菌剂, Schurek 等[23]利用 DART 结合 TOF-MS 和 DESI 离子源结合线性离子阱串联 MS 在 1 min 之内实现了对小麦中噻球果伞素类杀菌剂的快速筛查。利用杀菌剂咪鲜胺做内标物, 可实现对杀菌剂在 0.005~0.03 mg/kg 范围内的定量分析。除此之外, 还有报道将 DART-MS 用于蜂蜜中 5-羟甲基糠醛[24]、水中污染物[25]和防紫外线物质[26]、米糠中次氯酸钠氧化产物[27]、油脂食品中有机磷杀虫剂[28]、含甘油食物中乙烯乙二醇和二甘醇[29]、饲料中抗寄生虫药[30]、奶制品和肥肉中异丙基硫杂蒽酮[31]、食物中邻苯二甲酸盐[32]、蔬菜油当中 3-氯-1,2-丙二醇等[33]物质的快速筛查和定量分析。其他 AMS 技术在食品中有毒有害物质的检测上也有重要的应用。Garcia-Reyes 等[34]通过 DESI 对果皮或蔬果萃取物中残留的 16 种具有代表性的农用化学品(化肥、杀虫剂、除草剂、杀菌剂)进行分析, 以番茄或橘子萃取物为例, 检出限从 1~90 μg/kg 不等, 低于欧盟对其中大多数物质规定的最高残留限。为了对食品生产中产生的副产物 4-甲基咪唑进行检测, Li 等[35]利用纸喷雾离子源结合三重四级杆 MS 对其进行定性定量分析, 能检测出焦糖萃取液中低至 3 pg/μL 的 4-甲基咪唑。Luosujarvi 等[36]则利用 DAPPI-MS 鉴定了橙皮上的杀菌剂抑霉唑, 展示了 DAPPI-MS 在食品安全快速筛查中有很好地应用前景。

5　食品质量监控

利用敞开式离子化质谱, 可实现对食品中掺杂物质的快速筛查, 对引导消费者消费有重要的意义。Vaclavik 等[37]利用 DART-TOF-MS, 通过对甲醇-水萃取物中三酰基甘油类物质(triacylglycerols, TAGs)和极性化合物的分析对橄榄油的品质进行了区分。根据油中 TAGs 物质在 MS 中形成的碎片离子及其相对强度很容易区分特级初榨橄榄油、橄榄油渣、橄榄油(初榨橄榄油和精炼橄榄油的混合物)和以次充好的榛子油。利用线性判别分析算法(linear discriminant analysis, LDA), 通过对其中极性化合物的指纹图谱分析, 可检测出掺杂有 6%榛子油的橄榄油。真假食用肉桂中香豆素含量存在巨大差异, 真肉桂中香豆素含量为 0.004%, 而在假肉桂中则高达 1%。Avula 等[38]利用 DART-QTOF-MS 对真假肉桂中香豆素及其他物质进行分析, 结合对数据进行主成分分析(principal component analysis, PCA), 成功区分市售真假肉桂。Hrbek 等[39]则利用 DART-MS 对乳制品中掺杂的植物油进行检测, 同样根据对 TAG 类物质的谱图鉴定, 结合 PCA 和 LDA 数据分析, 能检测乳酪中掺杂低至 1%的植物油。除此之外, 作者分别将新鲜菜籽油和被氧化菜籽油(120 ℃条件下加热 6 h)掺杂进乳酪中, 根据质谱中 TAG 类物质加和离子峰的不同进一

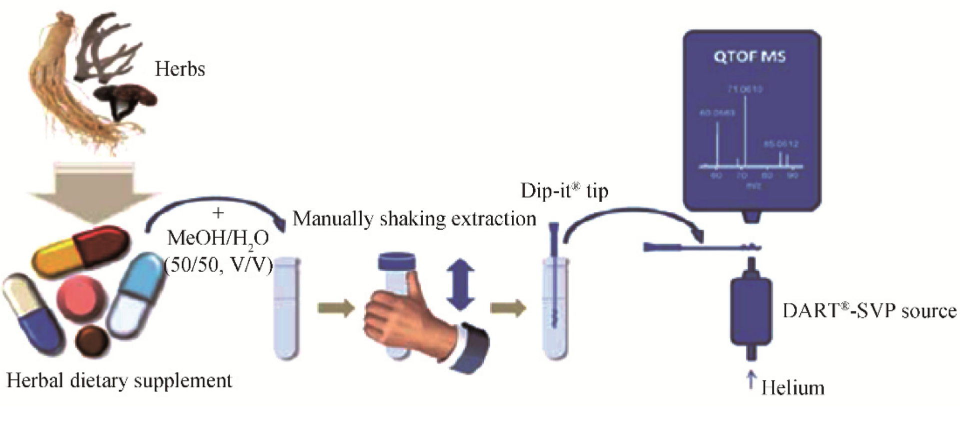

图 2 基于 DART-MS 的中药保健品中非法添加西药成分的筛查分析流程示意图[21]
Fig. 2Screening process of synthetic antidiabetic drug adulteration in herbal supplement[21]

步区分掺杂菜籽油的优劣(见图 3)。另外, 还有将 DART 应用于猪油牛油相互掺杂[40]、特拉普啤酒(Trappist Beers)[41]和抗痢疾药物的真假鉴定[42]、乌头炮制过程监测[43]、传统中药丹参的质量监控[44]中。Hartmanova 等[45]利用 nano-DESI 筛查红酒中的花色苷成分。通过对酒中花色苷成分的分析, 可以快速鉴别不同品种酒之间的相互掺杂以及用接骨木提取物染色的酒。Montowska 等[46]则利用敞开式液液萃取表面分析质谱(liquid extraction surface analysis mass spectrometry, LESA-MS)分析加工牛肉、猪肉等多种肉类中的蛋白质和多肽成分, 通过对不同肉质之间蛋白组和多肽组的分析, 可以区分不同肉类的掺杂。在对餐厨回收油和食用油掺杂方面, Zhou 等[47]引入中性解吸(neutral desorption, ND)样品装置结合 DBDI-MS 通过对油中的游离脂肪酸等一系列代表性物质进行分析, 成功区分食用油中掺杂的餐厨回收油成分。

6 食品组成成分分析

除了用于鉴定食品中的非法添加、有毒有害成分外, DART 也适用于分析食品的某些组成成分。植物激素在植物的发育、生长、成熟、凋零过程中都起着重要作用, 但常用的液相色谱-质谱联用(liquid chromatography-mass spectrometry, LC-MS)、气相色谱-质谱联用(gas chromatography-mass spectrometry, GC-MS)方法耗时长, 不适用于高通量分析。Liu 课题组[48]用简单的单液滴液/液/液微萃取(single-drop liquid-liquid-liquid microextraction, SD-LLLME)对果汁样品进行提取后, 用 DART-MS, 建立了果汁中 6 种植物激素的同时分析方法。检出限为 0.65~0.72 ng/mL, 并有较好的线性(r^2=0.991~0.996), 最后实现了对鲜榨菠萝汁、梨汁、西瓜汁中植物激素的快速检出。此外, 该课题组还利用 DART-MS 原位快速鉴别茶叶品质[49]。在正、负离子全扫描模式下, 对 8 种茶叶中茶氨酸、咖啡碱等物质进行 MS 分析, 根据这些活性成分含量的不同, 可区分茶叶的优劣。异黄酮是广泛存在于大豆当中的一种植物激素, 有降低胆固醇、延缓衰老的作用。Lojza 等[50]利用 DART-MS 对大豆中的异黄酮类物质进行定量分析, 检出限为 5 mg/kg。Morlock 等[51]结合高效薄层色谱和 DART-MS 对蜂胶中酚类化合物进行鉴定以区分不同产地的 64 种天然蜂胶, 并将该分析方法用于产地不明的 27 种蜂胶进行分析。此外, AMS 在大蒜、洋葱中刺激性气味成分[52]、五味子中木酚素[53]以及姜黄中姜黄素分布[54]的鉴定中也有应用。

7 监测食品中的化学反应

Vaclavik 等[55]利用传动模式的 DART 离子源结合高分辨 MS 对 4 种植物油(橄榄油、油菜籽油、大豆油、葵花籽油)在加热过程中的化学物质变化进行了探究。通过对被加热和未被加热植物油中一系列物质如三酰基甘油、植物甾醇、游离脂肪酸以及它们的氧化产物的 MS 数据进行分析, 探究了植物油在氧化过程中所含化学物质含量的变化。此外, 他们利用同样的方法对不同烘焙方式下饼干中产生的丙烯酰胺进行了测定[56]。丙烯酰胺是富含淀粉的食物在加热后, 其中的天冬酰胺、还原糖或羰基物质通过美拉德反应产生的, 是一类潜在的致癌物质。通过建立的 DART-MS 分析方法以及对数据进行多变量分析可做到对饼干烘焙过程中产生丙烯酰胺物质的实时监测, 用以减轻食品加工过程带来的污染。二十二碳六烯酸、二十碳五烯酸、亚麻酸

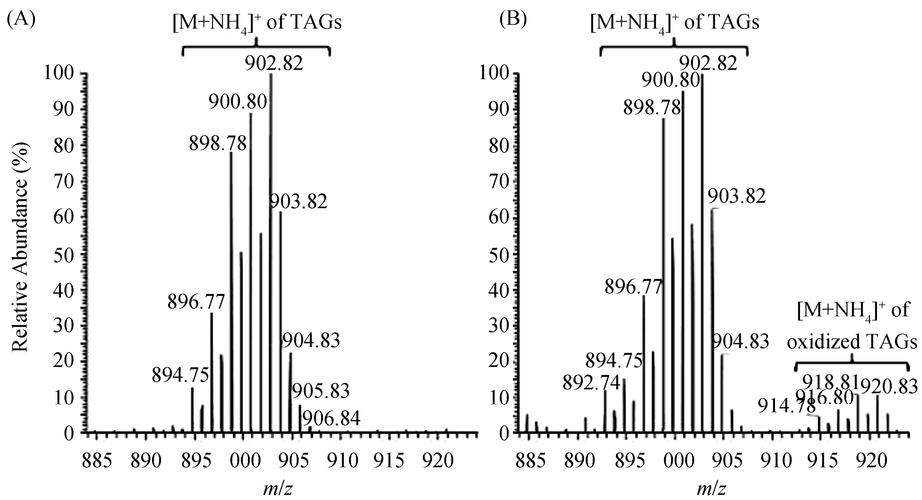

图 3 掺杂菜籽油的乳酪(10%, *V*:*V*)在正离子模式下的 DART-MS 图谱

Fig. 3DART-MS mass spectra of soft cheese adulterated with rapeseed oil (level 10%, *V*:*V*) recorded in positive ionization mode

注: (A): 新鲜菜籽油; (B): 被氧化的菜籽油(6 h, 120℃)[39]

Note: (A): fresh oil; (B): oxidized oil (6 h, 120℃) [39]

是具有重要生物学意义的欧米珈-3 脂肪酸, 有助于预防神经退行性疾病, 经常用于食品保健品中。然而欧米珈-3 脂肪酸的自氧化会导致食物腐败, 使其流失营养成分, 所以对其氧化过程的监控十分重要。West 等[57]利用 DESI-MS 以及 ESI-MS 对其氧化过程进行了监控, 发现在负离子模式下, 两者的谱图相似, 在对狗粮表面欧米珈-3 脂肪酸氧化过程的监控中, DESI-MS 与 ESI-MS 相比, 具有实时、原位、无需样品前处理的优点, 因而更具竞争力。

8 结论

AMS 技术为我们提供了一种快速、简便、能对食品中不同成分进行高通量分析的方法[58,59]。在食品中霉菌毒素类物质的检测、食品中非法添加物的快速筛查、食品本身有毒有害物质的鉴定、食品质量监控、食品组成成分分析和监测食品中的化学反应等方面有着重要的应用。与食品分析中传统的分离分析方法如 LC-MS 和 GC-MS 相比, 尽管灵敏度有待提高, 但是它能在大气压环境中对食品表面直接进行分析, 无需或只需简单的样品前处理步骤, 大大缩短了分析时间, 并可进行原位监测, 不失为快速筛查的一种有效方法。然而, 由于样品前处理步骤的省略, 食品本身的基质效应可能对 AMS 分析带来一定的干扰, 严格的质量监控体系对于 DART-MS 分析方法必不可少。鉴于此, 结合固相萃取(solid phase extraction, SPE)[60]和固相微萃取(solid phase microextraction, SPME)[61]等高效样品处理技术, 以及薄层色谱(thin layer chromatography, TLC)等一些简单的分离手段, 能够大大降低基质效应, 有利于获得背景信号低的图谱。另一方面, 采用内标法进行分析或者与高分辨 MS 以及串级 MS 的联用可提供更准确可靠的定性定量分析结果, 有助于减少假阳性现象。此外, 采用新的敞开式离子化技术如等离子体辅助激光解吸附离子化(plasma assisted multi-wavelength laser desorption, PALDI)[62]和敞开式表面辅助激光解吸附离子化(surface-assisted laser desorption ionization, SALDI)[63]技术进一步提高 AMS 的检测灵敏度也是很有意义的研究方向。

参考文献

[1] Takats Z, Wiseman JM, Gologan B, *et al*. Mass spectrometry sampling under ambient conditions with desorption electrospray ionization [J]. Science, 2004,306(5695): 471–473.

[2] Cody RB, Laramee JA, Durst HD. Versatile new ion source for the analysis of materials in open air under ambient conditions [J]. Anal Chem, 2005,77(8): 2297–2302.

[3] Na N, Zhao MX, Zhang SC, *et al*. Development of a dielectric barrier discharge ion source for ambient mass spectrometry [J]. J Am Soc Mass Spectr, 2007,18(10): 1859–1862.

[4] Haapala M, Po lJ, Saarela V, *et al*. Desorption atmospheric pressure photoionization [J]. Anal Chem, 2007,79(20): 7867–7872.

[5] Hajslova J, Cajka T, Vaclavik L. Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis [J]. Trac-Trends AnalChem, 2011,30(2): 204–218.

[6] Sisco E, Forbes TP. Rapid detection of sugar alcohol precursors and corresponding nitrate ester explosives using direct analysis in real time mass spectrometry[J]. Analyst, 2015,140(8): 2785–2796.

[7] Clemons K, Dake J, Sisco E, *et al*. Trace analysis of energetic materials via direct analyte-probed nanoextraction coupled to direct analysis in real time mass spectrometry[J]. Forensic SciInt, 2013,231(1–3): 98–101.

[8] Manova RK, Joshi S, Debrassi A, *et al*. Ambient surface analysis of organic monolayers using direct analysis in real time orbitrap mass spectrometry[J]. Anal Chem, 2014, 86(5): 2403–2411.

[9] Yu SX, Crawford E, Tice J, *et al*. Bioanalysis without sample cleanup or chromatography: the evaluation and initial implementation of direct analysis in real time ionization mass spectrometry for the quantification of drugs in biological matrixes[J]. Anal Chem, 2009,81(1): 193–202.

[10] Busman M, Liu JH, Zhong HJ, *et al*. Determination of the aflatoxin AFB1 from corn by direct analysis in real time-mass spectrometry (DART-MS)[J]. Food AdditContam Part A-Chem, 2014,31(5): 932–939.

[11] Busman M, Bobell JR, Maragos CM. Determination of the aflatoxin M-1 (AFM(1)) from milk by direct analysis in real time - mass spectrometry (DART-MS)[J]. Food Control, 2015,47: 592–598.

[12] Vaclavik L, Zachariasova M, Hrbek V, *et al*. Analysis of multiple mycotoxins in cereals under ambient conditions using direct analysis in real time (DART) ionization coupled to high resolution mass spectrometry[J]. Talanta, 2010,82(5): 1950–1957.

[13] Shen Y, Van Beek TA, ClaassenFW,*et al*. Rapid control of Chinese star anise fruits and teas for neurotoxic anisatin by direct analysis in real time high resolution mass spectrometry[J]. J Chromatogr A, 2012,1259: 179–186.

[14] Maragos CM, Busman M. Rapid and advanced tools for mycotoxin analysis: a review[J]. Food AdditContam Part A-Chem, 2010,27(5): 688–700.

[15] Vaclavik L, Rosmus J, Popping B, *et al*. Rapid determination of melamine and cyanuric acid in milk powder using direct analysis in real time-time-of-flight mass spectrometry[J]. J Chromatogr A, 2010,1217(25): 4204–4211.

[16] Zhang LY, Yong W, Liu JH, *et al*. Determination of dicyandiamide in powdered milk using direct analysis in real time quadrupole time-of-flight tandem mass spectrometry[J]. J Am Soc Mass Spectrom, 2015,26(8): 1414–1422.

[17] Yang SP, Ding JH, Zheng J, *et al*. Detection of melamine in milk products by surface desorption atmospheric pressure chemical ionization mass spectrometry[J]. Anal Chem, 2009,81(7): 2426–2436.

[18] Li Z, Zhang YW, Zhang YD, *et al*. Rapid analysis of four Sudan dyes using direct analysis in real time-mass spectrometry[J]. Anal Methods, 2015,7(1): 86–90.

[19] Chen HW, Zhang X, Luo MB. Desorption electrospray ionization mass spectrometry for fast detection of Sudan dyes in foods without sample pretreatment[J]. Chin J Anal Chem, 2006,34(4): 464–468.

[20] Taverna D, Di Donna L, Mazzotti F, *et al*. High-throughput determination of Sudan Azo-dyes within powdered chili pepper by paper spray mass spectrometry[J]. J Mass Spectrom, 2013,48(5): 544–547.

[21] Zhou ZG, Zhang JL, Zhang W, *et al*. Rapid screening for synthetic

antidiabetic drug adulteration in herbal dietary supplements using direct analysis in real time mass spectrometry[J]. Analyst, 2011,136(12): 2613−2618.

[22] Farre M, Pico Y, Barcelo D. Direct peel monitoring of xenobiotics in fruit by direct analysis in real time coupled to a linear quadrupole ion trap-orbitrap mass spectrometer[J]. Anal Chem, 2013,85(5): 2638−2644.

[23] Schurek J, Vaclavik L, Hooijerink H, *et al*. 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[J]. Anal Chem, 2008,80(24): 9567−9575.

[24] Chernetsova ES, Morlock GE. Assessing the capabilities of direct analysis in real time mass spectrometry for 5-hydroxymethylfurfural quantitation in honey[J]. Int J Mass Spectrom, 2012,314: 22−32.

[25] Dwivedi P, Gazda DB, Keelor JD, *et al*. Electro-thermal vaporization direct analysis in real time-mass spectrometry for water contaminant analysis during space missions[J]. Anal Chem, 2013,85(20): 9898−9906.

[26] Haunschmidt M, Klampfl CW, Buchberger W, *et al*. Determination of organic UV filters in water by stir bar sorptive extraction and direct analysis in real-time mass spectrometry[J]. Anal BioanalChem, 2010,397(1): 269−275.

[27] Wang SZ, Fan X, Zheng AL,*et al*.Evaluation of the oxidation of rice husks with sodium hypochlorite using gas chromatography-mass spectrometry and direct analysis in real time-mass spectrometry[J]. Anal Lett, 2014,47(1): 77−90.

[28] Kiguchi O, Oka K, Tamada M, *et al*. Thin-layer chromatography/direct analysis in real time time-of-flight mass spectrometry and isotope dilution to analyze organophosphorus insecticides in fatty foods[J]. J Chromatogr A, 2014,1370: 246−254.

[29] Self RL. Direct analysis in real time-mass spectrometry (DART-MS) for rapid qualitative screening of toxic glycols in glycerin-containing products[J]. J Pharm Biomed Anal, 2013,80: 155−158.

[30] Martinez-Villalba A, Vaclavik L, Moyano E, *et al*. Direct analysis in real time high-resolution mass spectrometry for high-throughput analysis of antiparasitic veterinary drugs in feed and food[J]. Rapid Commun Mass Spectr, 2013,27(3): 467−475.

[31] Morlock G, Schwack W. Determination of isopropylthioxanthone (ITX) in milk, yoghurt and fat by HPTLC-FLD, HPTLC-ESI/MS and HPTLC-DART/MS[J]. Anal BioanalChem, 2006,385(3): 586−595.

[32] Self RL, Wu WH. Rapid qualitative analysis of phthalates added to food and nutraceutical products by direct analysis in real time/orbitrap mass spectrometry[J]. Food Control, 2012,25(1): 13−16.

[33] MoravcovaE, Vaclavik L, Lacina O, *et al*. Novel approaches to analysis of 3-chloropropane-1,2-diol esters in vegetable oils[J]. Anal Bioanal Chem, 2012,402(9): 2871−2883.

[34] Garcia-Reyes JF, Jackson AU, Molina-Diaz A, *et al*. Desorption electrospray ionization mass spectrometry for trace analysis of agrochemicals in food[J]. Anal Chem, 2009,81(2): 820−829.

[35] Li AY, Wei P, Hsu HC, *et al*. Direct analysis of 4-methylimidazole in foods using paper spray mass spectrometry[J]. Analyst, 2013,138(16): 4624−4630.

[36] Luosujarvi L, Kanerva S, Saarela V, *et al*. Environmental and food analysis by desorption atmospheric pressure photoionization-mass spectrometry[J]. Rapid Commun Mass Spectr, 2010,24(9): 1343−1350.

[37] Vaclavik L, Cajka T, Hrbek V, *et al*.Ambient mass spectrometry employing direct analysis in real time (DART) ion source for olive oil quality and authenticity assessment[J]. Anal ChimActa, 2009,645(1−2): 56−63.

[38] Avula B, Smillie TJ, Wang YH, *et al*. Authentication of true cinnamon (Cinnamon verum) utilising direct analysis in real time (DART)-QToF-MS [J]. Food AdditContam Part A-Chem, 2015,32(1): 1−8.

[39] Hrbek V, Vaclavik L, Elich O, *et al*.Authentication of milk and milk-based foods by direct analysis in real time ionization-high resolution mass spectrometry (DART-HRMS) technique: A critical assessment[J]. Food Control, 2014,36(1): 138−145.

[40] Vaclavik L, Hrbek V, Cajka T, *et al*. Authentication of animal fats using direct analysis in real time (dart) ionization-mass spectrometry and chemometric tools[J]. J Agric Food Chem, 2011,59(11): 5919−5926.

[41] Cajka T, Riddellova K, Tomaniova M, *et al*. Ambient mass spectrometry employing a DART ion source for metabolomic fingerprinting/profiling: a powerful tool for beer origin recognition[J]. Metabolomics, 2011,7(4): 500−508.

[42] Fernandez FM, Cody RB, Green MD,*et al*. Characterization of solid counterfeit drug samples by desorption electrospray ionization and direct-analysis-in-real-time coupled to time-of-flight mass spectrometry[J]. ChemMedChem, 2006,1(7): 702−705.

[43] Zhu HB,Wang CY, Qi Y, *et al*. Rapid quality assessment of Radix AconitiPreparata using direct analysis in real time mass spectrometry[J]. Anal ChimActa, 2012,752: 69−77.

[44] Zeng SS, Wang L, Chen T, *et al*. Direct analysis in real time mass spectrometry and multivariate data analysis: A novel approach to rapid identification of analytical markers for quality control of traditional Chinese medicine preparation[J]. Anal ChimActa, 2012,733: 38−47.

[45] Hartmanova L, Ranc V, Papouskova B, *et al*. Fast profiling of anthocyanins in wine by desorption nano-electrospray ionization mass spectrometry[J]. J Chromatogr A, 2010,1217(25): 4223−4228.

[46] Montowska M, Alexander MR, Tucker GA, *et al*. Authentication of processed meat products by peptidomic analysis using rapid ambient mass spectrometry[J]. Food Chem, 2015,187: 297−304.

[47] Zhou YF, Wu ZC, Li C, *et al*. Coupling neutral desorption sampling to dielectric barrier discharge ionization mass spectrometry for direct oil analysis[J]. Anal Methods, 2014,6(5): 1538−1544.

[48] Bai Y, Zhang JL, Bai Y, *et al*. Direct analysis in real time mass spectrometry combined with single-drop liquid-liquid-liquid microextraction for the rapid analysis of multiple phytohormones in fruit juice[J]. Anal BioanalChem, 2012,403(8): 2307−2314.

[49] Zhang JL, Zhang W, Zhou ZG, *et al*. In situ and rapid identification of tea by direct analysis in real time mass spectrometry[J]. ChinJ Chromatogr, 2011,29(7): 681−686.

[50] Lojza J, Cajka T, Schulzova V, *et al*. Analysis of isoflavones in soybeans employing direct analysis in real-time ionization-high-resolution mass spectrometry[J]. J Sep Sci, 2012,35(3): 476−481.

[51] Morlock GE, Ristivojevic P, Chernetsova ES. Combined multivariate data analysis of high-performance thin-layer chromatography fingerprints and direct analysis in real time mass spectra for profiling of natural products like propolis[J]. J Chromatogr A, 2014,1328: 104−112.

[52] Block E, Dane AJ, Thomas S, *et al*. Applications of direct analysis in real time mass spectrometry (dart-MS) in allium chemistry. 2-propenesulfenic

and 2-propenesulfinic acids, diallyltrisulfane s-oxide, and other reactive sulfur compounds from crushed garlic and other alliums[J]. JAgric Food Chem, 2010,58(8): 4617–4625.

[53] Kim HJ, Oh MS, Hong J, *et al*. Quantitative analysis of major dibenzocyclooctanelignans in schisandraefructus by online TLC-DART-MS[J]. Phytochem Anal, 2011,22(3): 258–262.

[54] Rahman A, Angawi RF, Kadi AA. Spatial localisation of curcumin and rapid screening of the chemical compositions of turmeric rhizomes (*Curcuma longa* Linn.) using direct analysis in real time-mass spectrometry (DART-MS)[J]. Food Chem, 2015,173: 489–494.

[55] Vaclavik L, Belkova B, Reblova Z, *et al*. Rapid monitoring of heat-accelerated reactions in vegetable oils using direct analysis in real time ionization coupled with high resolution mass spectrometry[J]. Food Chem, 2013,138(4): 2312–2320.

[56] Vaclavik L, Capuano E, Gokmen V, *et al*. Prediction of acrylamide formation in biscuits based on fingerprint data generated by ambient ionization mass spectrometry employing direct analysis in real time (DART) ion source[J]. Food Chem, 2015,173: 290–297.

[57] West RE, Marvin RK, Hensley K, *et al*. Qualitative analysis of omega-3 fatty acid oxidation by desorption electrospray ionization-mass spectrometry (DESI-MS)[J]. Int J Mass Spectrom, 2014,372: 29–38.

[58] Li LP, Feng BS, Yang J, *et al*.Applications of ambient mass spectrometry in high-throughput screening[J]. Analyst, 2013, 138(11): 3097–3103.

[59] 冯鲍盛, 白玉, 刘虎威. 实时直接分析质谱新技术及其应用[J]. 中国科学-化学, 2014, 44: 784–788.

Feng BS, Bai Y, Liu HW. New techniques of direct analysis in real time-mass spectrometry andtheir applications [J]. Sci Sin Chim, 2014, 44: 784–788.

[60] Li XJ, Wang X, Li LN, *etal*.Direct analysis in real time mass spectrometry: a powerful tool for fast analysis[J]. Mass Spectr Lett, 2015, 6: 1–6.

[61] Wang X, Li XJ, Li Z, *et al*. Online coupling of in-tube solid-phase microextraction with direct analysis in real time mass spectrometry for rapid determination of triazine herbicides in water using carbon-nanotubes-incorporated polymer monolith[J]. Anal Chem, 2014, 86(10):4739–4747.

[62] Zhang JL, Zhou ZG, Yang JW, *et al*.Thin layer chromatography/plasma assisted multi-wavelength laser desorption ionization mass spectrometry for facile separationmand selective identification of low molecular weight compounds [J]. Anal Chem, 2012, 84(3): 1496–1503.

[63] Zhang JL, Li Z, Zhang CS, *et al*. Graphite coated paper as substrate for high sensitive analysis in ambient surface-assisted laser desorption/ionization mass spectrometry [J]. Anal Chem, 2012, 84(7): 3296–3301.

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