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Ambient mass spectrometry for food science and industry

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ABSTRACT

Ambient mass spectrometry (AMS) allows direct molecular characterization of various raw food samples with minimal or no sample pretreatment. Because of the excellent sensitivity and specificity of analysis, AMS has been increasingly applied in food science and industry. In virtually, any type of food samples including solid, liquid, viscous, and bulk food samples could be directly analyzed using mass spectrometry powered by versatile ambient ionization techniques. Moreover, mass spectrometry imaging (MSI) offers a unique opportunity to explore the spatial-chemical information from numerous food samples. Herein, the principle of AMS, typical instrumental setup, and applications in different type of food samples are systematically reviewed, the advantages and shortages of AMS for food analysis are mentioned, and the impact and challenge of AMS on food science are briefly discussed.

1. Introduction

Food is a basic human necessity and essential for a sustainable world, thus the food safety is of paramount importance to global economy, human health and homeland security [1,2]. With the growth of global population, the increasing demand for food has led to corresponding growth of the whole food science and industry. Yet motivated by the maximization of profits, food safety incidents occurred frequently [3]. For example, the U.S. melamine scandal in 2007 [4], Irish pork crisis in 2008 [5], and the European horsemeat scandal in 2013 [3] caused great panic to public and society. Consequently, food quality and safety is of increasing concern in recent years [6]. However, owing to diversity and chemical complexity of food samples, trace levels of miscellaneous analytes including microbial pathogens, heavy metals, food additives, biotoxins, agrichemicals residues, food package migrants, illicit adulterants, persistent organic pollutants, etc., [1,6] make the food safety analysis a great challenge in modern society. Though conventional technologies, such as liquid/gas chromatography-mass spectrometry (LC/GC-MS) [7–11], enzyme-linked immunosorbent assay (ELISA) [12,13] and so on, could achieve the detection of specific compounds within food samples, generally accompanied with a series of tedious sample pretreatment procedures (e.g., gradation, extraction, enrichment, separation). Particularly, the above-mentioned methods may not be suitable for the direct and high-throughput analysis of real food samples in contemporary food science and industry. Therefore, it's urgently demanded to develop efficient and powerful tools for the study of various types of complex food samples.

Mass spectrometry (MS) is one of the most versatile technologies for the analysis of foods, beverages as well as food contact materials for processing or packaging [14], with advantages of high sensitivity, high selectivity, and least response time. Since the invention of desorption electrospray ionization mass spectrometry (DESI-MS), high-throughput analysis under an open atmosphere was pioneered by Cooks et al. in 2004 [15]. Following by DESI, more than 40 kinds of typical ambient ionization techniques, such as desorption atmospheric pressure chemical ionization (DAPCI) [16], direct analysis in real time (DART) [17], extractive electrospray ionization (EESI) [18], dielectric-barrier-discharge ionization (DBDI) [19], and low-temperature plasma (LTP) [20] etc. were developed to analyze a variety of complex matrices samples. Due to the merits of simplicity, cost-efficiency, and high-throughput of analysis, AMS techniques have been increasingly applied in food science and industry. In virtually any type of food samples could be

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directly analyzed using one of the currently available ambient ionization techniques.

Typically, trace amounts of analytes on solid foods could be rapidly detected using either DESI-MS, DART-MS or DAPCI-MS [21,22], etc. Both volatile and non-volatile analytes could be detected by ambient ionization techniques for surface analysis. Laser, heat, solvent extraction or gas liberation would be preferably used during the desorption/ionization (DI) process for the detection of chemicals with low volatility [23,24], particularly on viscous food surfaces (e.g., cheese, honey, oils). Alternatively, liquid and gaseous samples could be real-time monitored using EESI and its derivative technique, while bulk food samples could be qualitatively and quantitatively analyzed through internal extractive electrospray ionization mass spectrometry (iEESI-MS) [25–27]. Besides, the development of MSI has further extended the application scopes of AMS in food science, which was particularly helpful for food quality control. In this review, the principle of AMS, typical instrumental setup, and applications in different type of food samples are systematically reviewed, the advantages and shortages of AMS for food analysis are mentioned, and the impact and challenge of AMS on food industry are briefly discussed.

2. Typical ionization methods

In general, there are mainly three classes of ambient ionization methods based upon different type of samples: (1) direct ionization methods for solid samples; (2) direct ionization methods for liquid/viscous samples; (3) direct ionization methods for bulk samples.

2.1. Direct ionization methods for solid samples

Direct ionization techniques for solid samples are a series of DI techniques. The condensed phase-to-gaseous ion transfer that is a main feature of DI techniques is achieved by different primary ions [15], and DI techniques can be classed into three groups based upon generation mechanisms of primary ions. (1) Spray ionization (electrospray/sonic spray) techniques such as DESI [15] (Fig. 1a), electrospray laser desorption/ionization (ELDI) [28], laser ablation electrospray (LAESI) [29], matrix-assisted laser desorption electrospray (MALDESI) [30], infrared laser assisted desorption electrospray (IRLADESI) [31], neutral desorption extractive electrospray ionization (ND-EESI) [32], and easy ambient sonic spray ionization (EASI) [33] etc.; (2) electric field ionization (electron/plasma) techniques such as DAPCI [16] (Fig. 1b), DART [17] (Fig. 1c), thermal desorption atmospheric pressure chemical ionization (TDAPCI) [34], ambient solid analysis probe (ASAP) [35], DBDI [19], LTP [20] (Fig. 1d), atmospheric pressure glow discharge desorption ionization (APGDDI) [36], helium atmospheric pressure glow discharge ionization (HAPGDI) [37] and microwave plasma torch desorption (MPT) [38] etc.; (3) gas-, heat- or laser-assisted ionization techniques including thermal desorption chemical ionization (TDCI) [39], atmospheric pressure thermal discharge ionization (APTDI) [40], laser diode thermal desorption (LDTD) [41], desorption atmospheric pressure photo ionization (DAPPI) [42], and atmospheric pressure laser discharge ionization (APLDI) [43], etc. Detailed mechanisms of these techniques will not be included here, which could be found in several reviews [44–46].

2.2. Direct ionization methods for liquid/viscous samples

In principle, the analyzed sample of the above-mentioned DI techiniques is presented as a solid, but the physical state of the original sample can also be different [47,48]. Motivated by the need for direct analysis of liquid samples with complex matrices, various AMS methods such as electrosonic spray ionization (ESSI) [49], surface sampling probe (SSP) [50], fused droplet electrospray ionization (FDESI) [51], EESI [52], and paper spray (PS) [53,54], direct inlet probe-atmospheric-pressure chemical ionization (DIP-APCI) [55,56], direct inlet probe-electrospray ionization (DIP-ESI) [57], etc. have been developed.

Fig. 2 is schematic illustration of extraction and collision between microdroplets in EESI-MS. Unlike other AMS techniques, in EESI-MS, sample is isolated from electric field, and contamination derived from chemical regents is avoided at the maximum degree. The major features of EESI-MS includes: (1) real-time, online and remote monitoring; (2) *in vivo* analysis; (3) detection of both polar and non-polar compounds; (4) toleration of complex matrices; (5) no chemical contamination; (6) no tedious sample pretreatment; (7) chemical reaction system monitor such as ion/molecule or ion/ion reactions; (8) capable of investigating liquids, gases, aerosols, surfaces, etc.; (9) easy to be implemented on various instruments. Except for application in liquid samples analysis, EESI-MS has also performed satisfactorily *in vivo* metabolism analysis, providing a convenient tool to deeply probe into dynamics of human bodies by

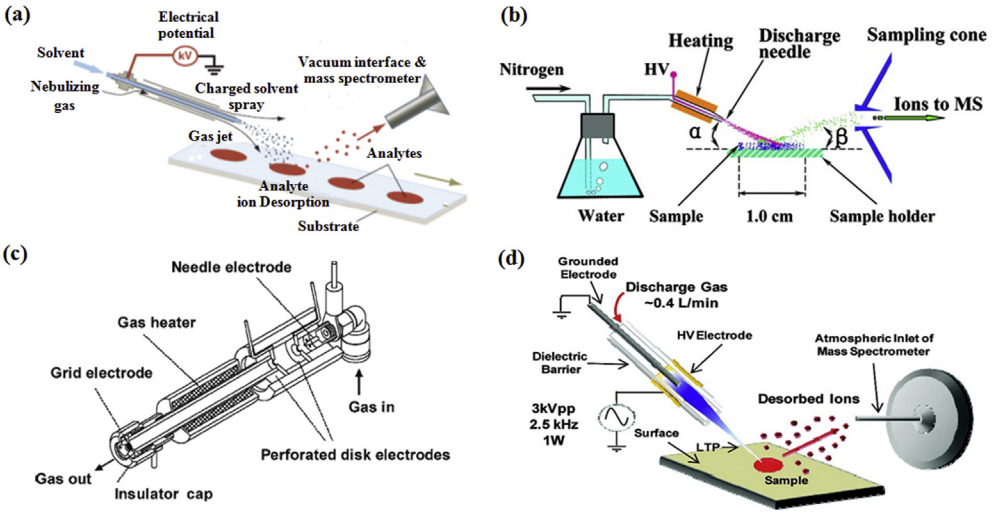

Fig. 1. Schematic illustrations of typical ambient ionization methods in solid food sample analysis. (a) DESI-MS (reprinted from [15] with the permission of AAAS/Science), (b) DAPCI-MS (reprinted from [16] with the permission of ACS), (c) DART-MS (reprinted from [17] with the permission of ACS) and (d) LTP-MS (reprinted from [20] with the permission of ACS).

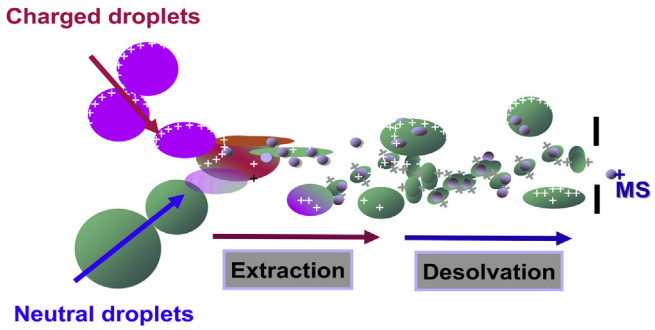

Fig. 2. Schematic illustration of extraction and collision between microdroplets in EESI-MS (reprinted from [61] with the permission of Elsevier).

fingerprinting both volatile and nonvolatile compounds in breath samples, and real-time determination of human pharmacokinetic profiles in a noninvasive and painless way [18,58,59]. Besides, in order to be conveniently implemented for *in situ* mass spectrometric analysis, a novel nanoextractive electrospray ionization (nanoEESI) source, requiring no sheath gas for either primary ion production or neutral sample introduction, has been developed for *in situ* analysis of various actual samples [60].

From the point of view of sample phase, EESI-MS was initially developed for direct and real-time monitoring of complex liquid samples [62]. For the interrogation of viscous samples, ND-EESI-MS was developed. ND-EESI-MS combined atmospheric pressure desorption sampling by a gentle stream of air or gas, followed by the neutral molecules transported to EESI source for efficient ionization, which showed obvious advantage in rapid analysis of complex viscous samples including oil, honey and so on [62–64]. Fig. 3 were the schematic diagrams of seven types of ND sampling devices for viscous sample analysis. Actually, except for ND-EESI-MS, laser diode thermal desorption-negative mode atmospheric pressure chemical ionization tandem mass spectrometry (LDTD-APCI-MS/MS) [65], neutral desorption sampling combined with DBDI-MS (ND-DBDI-MS) [66], easy ambient sonic-spray ionization mass spectrometry (ESAI-MS) [67], DESI-MS and DART-MS, etc., also could be used for viscous sample analysis.

2.3. Direct ionization methods for bulk samples

Field trials have already demonstrated that agrichemical residues are distributed inhomogeneously among individual samples [68,69], and for the real-world samples, the surface concentration of compounds can significantly differ from the bulk-phase concentration [70]. From these regards, above-mentioned AMS techniques for direct analysis of analytes on the surface of solid, liquid and viscous food samples would hardly meet the requirements of contemporary food safety and quality control. Importantly, current techniques usually require tedious sample pretreatments to obtain molecular information from the three-dimensional (3-D) volume of a bulk sample, and the processes are commonly associated with biological degradation, chemical reactions, material loss and reagents contaminants [27]. To resolve these problems and profile clear volumetric information of molecules within the bulk food samples at molecular level without any sample pretreatment, a novel direct ionization technique, termed as iEESI-MS [25,26], was proposed. Fig. 4 was schematic illustration of iEESI-MS in bulk food sample analysis.

In iEESI-MS, the fused silica capillary was parallelly inserted into the bulk sample with a certain volume, allowing the distance between the fused silica capillary inserted the sample and the apex of sample was 2 mm. The apex of sample was then placed in front of the inlet of mass spectrometer at a distance of 5–6 mm. Extractive solutions (e.g., methanol, water) biased with high voltage is directly injected into the bulk sample through the capillary with a certain flow rate. The analytes were extracted by the infused extractive solvent and carried along the electric field gradient inside the bulk sample toward the adjacent mass spectrometer for interrogation. The unique features of iEESI-MS are as follows: (1) direct characterization of "internal" chemicals within bulk samples rather than on the surfaces; (2) solvent used can be easily changed, and ionization process controllability; (3) with minimal sample pretreatment; (4) no sheath gas; (5) high speed, sensitivity and specificity; (6) low sample consumption and simple operations; (7) easy to combine with different type of mass spectrometer. Currently, iEESI-MS has been successfully applied in multidiscipline such as plant metabolomics, food science and clinical diagnosis [25,27,70]. To sum up, the ionization mechanism of all described AMS systems are based on three ionization methods: ESI (e.g., DESI, EESI, DIP-ESI), APCI (e.g., DART, DAPCI, ASAP, APGDI, DIP-APCI), and APPI (e.g., DAAPPI) [71]. Table 1 shows available AMS techniques for different types of sample analysis.

3. Applications of AMS in different type of foods

Since various AMS techniques' introduction, numerous applications in forensic and pharmaceutical science have been

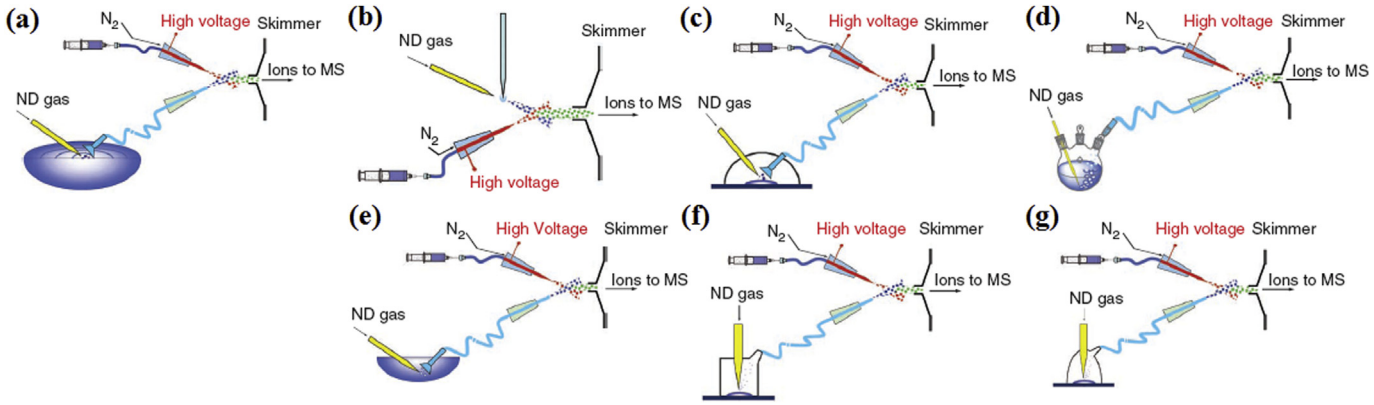

Fig. 3. Schematic diagrams of seven types of ND sampling devices of ND-EESI-MS in viscous sample analysis. (a) A typical open-air ND sampling device, (b) a simplified open-air ND sampling device, (c) a sealable ND sampling device, (d) a microjet ND sampling device, (e) a simplified microjet ND sampling device, (f) a typical GIND sampling device and (g) an improved GIND sampling device (reprinted from [64] with the permission of Nature).

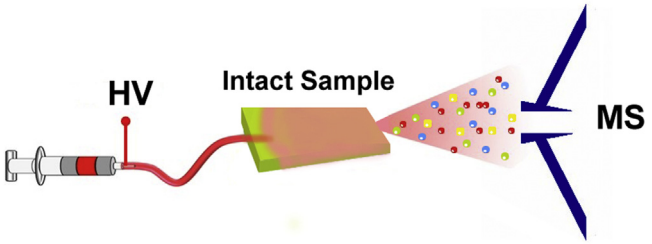

Fig. 4. Schematic illustration of iEESI-MS in bulk food sample analysis (reprinted from [27] with the permission of Springer Nature).

documented in earlier literatures [72–77]. Driven by the urgent demands for developments of powerful methods for high-throughput screening of multi-residues in complex samples [72], AMS techniques have been extensively applied to *in situ* analyze different type of food samples. In this section, the applications of AMS techniques in food science and industry from 2005 to date will be summarized according to different types of foods including solid foods, liquid foods, viscous foods, and bulk foods. Besides, the food imaging by AMS techniques was briefly introduced.

3.1. Solid foods

The aim of this section is mainly focused on the application of available AMS techniques in solid foods. Data are given for: (1) detection of regulated or functional compounds; (2) broadband chemical characterization; and (3) classification/authentication.

3.1.1. Detection of regulated or functional compounds

3.1.1.1. Agrichemicals. With greater control and tests being demanded by the authorities and food industry, AMS techniques play a key role in detection of a variety of trace food contaminants (e.g., agrichemicals, mycotoxins, illegal additives) and functional compounds from raw food samples. For example, DESI-MS was utilized for qualitative analysis of trace pesticides in food sample including mango, passion fruit, papaya and strawberries [78], and direct detection of 16 pesticides, insecticides, herbicides, and fungicides from fruit and vegetable [79]. Surface swabbing technique coupled with DART-MS was developed to rapidly screen the trace pesticides from the surfaces of fruits and vegetables (Fig. 5a) [80,81]. Also, DART-MS has been used for simultaneous analysis of organophosphorous insecticide in grapefruit [82]. Both DART-MS and DESI-MS have permitted a direct screening of strobilurin residues in wheat at concentration levels lower or closer to MRLs within 1min [83]. Besides, the coupling of nano-liquid chromatography with DBDI-MS was demonstrated to deliver high sensitivity in analysis of pesticides extracted using the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) approach from different matrices [84,85].

PS-MS is another AMS technique that has been used to analyze pesticides in various fruits and vegetables. For example, PS-MS could be used for fast screening of pesticides in oranges,

Table 1
The comparisons of various AMS techniques.

Number	Techniques	Abbreviation	Physical states of sample	Dominant sampling process	Publishing time (year)
1	Desorption electrospray ionization	DESI	S, L	Charged droplet jet surface desorption	2004
2	Surface sampling probe	SSP	S, L	Extraction using a neutral film on surface	2004
3	Sealing surface-sampling probe	SSSP	S, L		2004
4	Desorption atmospheric pressure chemical ionization	DAPCI	S, L	Gas ions jet desorption surface	2004
5	Ambient solid analysis probe	ASAP	S, L	Gas ions jet thermal desorption surface	2004
6	Atmospheric pressure laser matrix-assisted desorption Ionization	APMALDI	S, L	Gas jet with plasma desorption surface	2004
7	Fused Droplet Electrospray Ionization	FDESI	L	Extraction using a neutral liquid spray	2005
8	Electrospray Laser Desorption/Ionization	ELDI	S, L	Laser beam ablation/desorption	2005
9	Direct analysis in real time	DART	S, L, G	Gas ions jet desorption surface	2005
10	Thermal desorption atmospheric pressure chemical ionization	TDAPCI	S	Gas ions jet thermal desorption surface	2005
11	Laser ablation inductively coupled plasma	LA-ICP	S	Gas jet with plasma desorption surface	2005
12	Thermal desorption chemical ionization	TDCI	S, L	Organic salts ions thermal desorption	2005
13	Plasma assisted desorption ionization	PADI	S, L	Gas jet with plasma desorption surface	2006
14	extractive electrospray ionization	EESI	L, G	Extraction using a neutral liquid spray	2006
15	Desorption sonic spray ionization	DeSSI	S, L	Neutral high velocity spray desorption	2006
16	Matrix-assisted laser desorption electrospray	MALDESI	S, L	Matrix-assisted laser desorption	2006
17	Atmospheric pressure thermal discharge ionization	APTDI	S, L	Organic salts ions thermal desorption	2006
18	Neutral desorption extractive electrospray ionization	ND-EESI	S, C, L	Gas jet neutral desorption	2007
19	Laser ablation electrospray	LAESI	S, L	Laser beam ablation/desorption	2007
20	Dielectric discharge barrier ionization	DBDI	S, L	Gas jet with plasma desorption surface	2007
21	Desorption atmospheric pressure photo ionization	DAPPI	S, L		2007
22	Laser diode thermal desorption	LDTD	S, L	Laser diode desorption	2007
23	Atmospheric pressure glow discharge ionization	APGDI	S, L	Gas jet with plasma desorption surface	2008
24	Easy ambient sonic spray ionization	EASI	S, L	Neutral high velocity spray desorption	2008
25	Extractive atmospheric pressure chemical ionization	EAPCI	L, G	Gas ions extractive	2008
26	Jet desorption ionization	JeDI	S, L	Charged droplet jet surface desorption	2008
27	Low temperature plasma	LTP	S, L, G	Gas jet with plasma desorption surface	2008
28	Liquid microjunction surface-sampling probe	LMJSS	S, L	Extraction using a neutral film on surface	2008
29	Infrared laser assisted desorption electrospray	IRLADESI	S, L	Infrared laser assisted desorption	2009
30	Nano extractive electrospray ionization	NaoEESI	L	Extraction using a neutral liquid spray	2009
31	Atmospheric pressure laser discharge ionization	APLDI	S	Gas jet with plasma desorption surface	2009
32	Beta electron-assisted direct chemical ionization probe	BADCI	S	Beta electron-assisted direct chemical ionization	2009
33	Paper spray	PS	S, L	Extraction, transportation by electric field	2010
34	Air flow assisted ionization	AFAI	S, L, G	Charged droplet	2011
35	Internal extractive electrospray ionization	iEESI	S, L	Extraction using charged fine droplet	2013
36	Microwave plasma torch desorption	MPT	S, L, G	Gas jet with plasma desorption surface	2013

Note: S, L, G and C represent solid, liquid, gas and colloid.

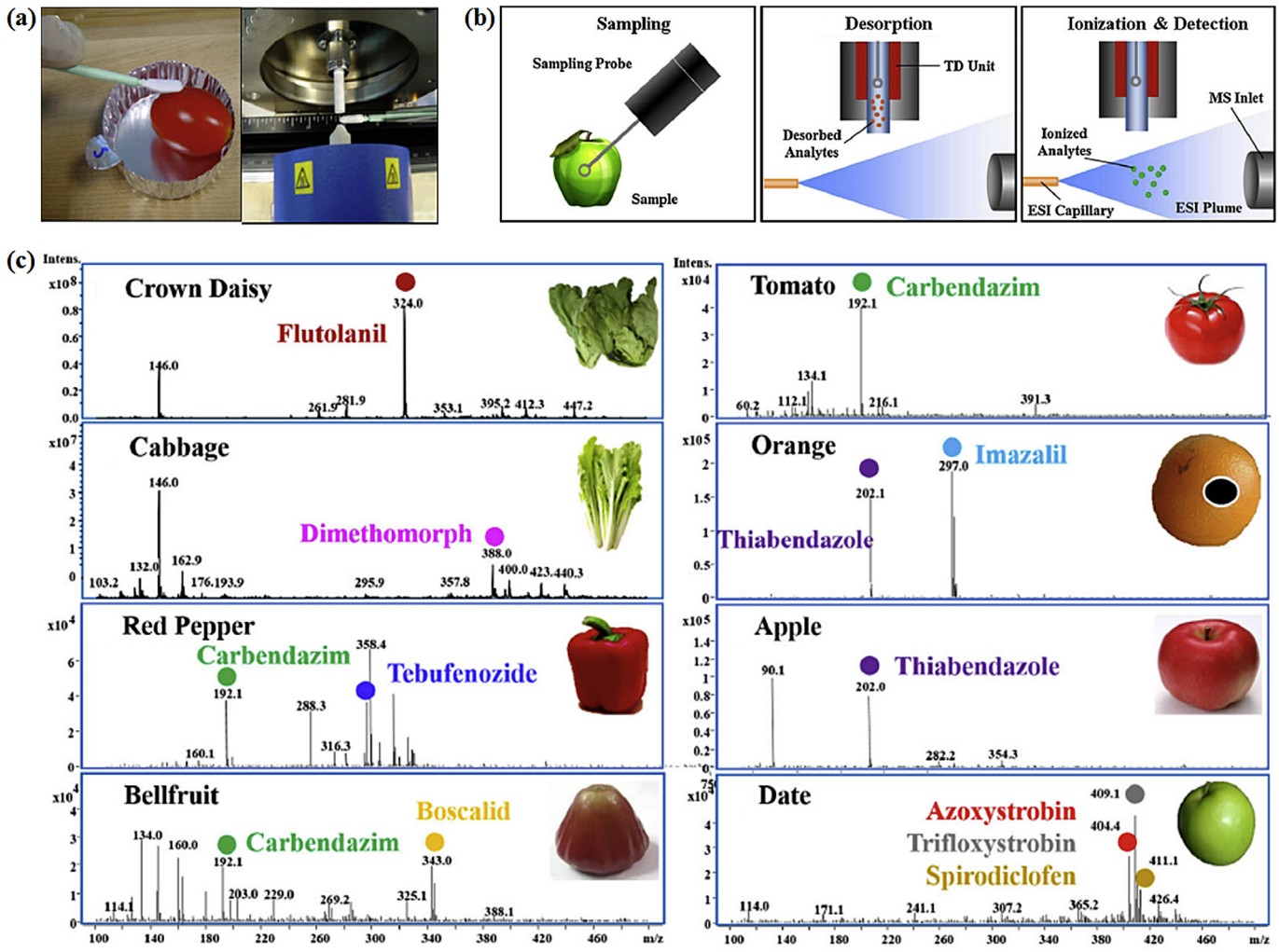

Fig. 5. Schematic diagrams of typical AMS techniques in agrichemicals analysis from solid foods. (a) Swabbing technique combined with DART-MS to directly sample and analyze pesticides from fruit and vegetable surface (reprinted from [81] with the permission of Springer), (b) TD-ESI-MS analytical procedure for residual pesticides on fruits and vegetables, and (c) TD-ESI-MS spectra of different fruits and vegetables (reprinted from [91] with the permission of Wiley).

grapefruits, lemons, limes, mandarins, tomatoes, apples, pears, strawberries, grapes and sweet peppers [86]. Using arugula, basil, cabbage, lettuce and kale as samples, the agrichemicals including atrazine, diuron and methomyl in low concentrations were analyzed by PS-MS and Leaf Spray Mass Spectrometry (LS-MS) [87]. In addition, liquid extraction surface analysis (LESA) coupled with infusion nano-electrospray high-resolution mass spectrometry was applied to the qualitative determination of pesticide residues on the surface of fruits and vegetables, and the results showed that pesticides, present at levels 20-fold below the usually allowed US Environmental Protection Agency (EPA) tolerance levels, are easily detected [88]. LTP-MS has been employed for screening of multi-class agrichemicals in fruits and vegetable, building an ideal tool for food industry to hand large quantities of contaminated fruit [89]. Microfabricated glow discharge plasma desorption/ionization mass spectrometry (MFGDP-MS) has been developed for direct screening of pesticide residues in fruits and vegetables *in situ* [90]. Also, thermal desorption electrospray ionization mass spectrometry (TD-ESI-MS) has achieved rapid screening of residual pesticides on fruits and vegetables (Fig. 5b and c) [91].

3.1.1.2. Mycotoxins. Mycotoxins in cereals are associated with serious acute toxicity and carcinogenicity in livestock and human, which has become an issue of great concern for decades worldwide [92,93]. With no complex sample pretreatments and high analysis speed, AMS methods have been much advantageous in mycotoxins analysis. For example, DART-MS was used for fast quantitative analysis of multiple mycotoxins isolated from wheat and maize by modified QuEChERS procedure [94], and aflatoxin AFB1 extracted from maize, further indicating that AMS could be applied to the developments of convenient quantitative assays of mycotoxins from feed relevant complex matrices [95]. Also, dispersive liquid-liquid microextraction coupled with direct electrospray probe tandem mass spectrometry (DEP-MS/MS) was used for the characterization of trace aflatoxin B1 in groundnuts, wheat and maize, showing the method is promising in providing significant toxicological information for food safety in the real world [96].

3.1.1.3. Illegal additives. Owing to food additives covered a wide range of chemical entities, including both natural and synthetic substances [97], hence another important application area of AMS methods in food science is the detection of illegal additives in complex food samples. For example, DESI-MS was employed for direct detection of Sudan dyes presented in chili powder [98], and rapid screening of veterinary drugs in cross-contaminated feed samples [99]. DART-MS has achieved high-throughput and fully

automated quantitative determination of melamine and cyanuric acid in milk powder [100]. Additionally, DAPCI-MS was used for direct detection of trace amounts of melamine in milk products [16] and pet foods [53] as well as cocaine in hot pot sauce materials [101]. PS-MS has achieved quantitative analysis of clenbuterol in beef, and LOD lower than 1 ng/g was achieved [102].

3.1.1.4. Functional compounds. Direct detection of functional compounds is of paramount significance in the development of natural products. Without any sample pretreatment, sinapine, a bioactive chemical usually presented in various seeds of *Brassica plants*, has been detected in radish taproot tissue through DAPCI-MS [103]. DART-MS has realized the direct detection of fungicides, antioxidants, and sugars in fruit peels [104], 2-propenesulfenic, 2-propenesulfinic acids, diallyl trisulfane s-oxide, and several reactive sulfur compounds from crushed garlic and other alliums [105], rapid quantitative analysis of caffeine in roasted ground coffee, instant coffee, and capsuled coffee [106], and identification of flavonoids and other phenolic compounds in propolis [107] as well as functional isoflavones compounds isolated from soybeans [108]. In addition, DESI-MS was efficiently used for qualitative analysis of omega-3 fatty acid oxidation in commercial dog kibbles [109], electrosonic spray ionization mass spectrometry (ESSI-MS) has achieved analysis of oligosaccharides and alpha hydroxy acids in fruits [110], and ESAI-MS provided a fast protocol to analyze triacylglyceride (TAG) in meats and fats [111].

3.1.2. Broadband chemical characterization

AMS techniques also act as a key role in broadband chemical characterization of food samples. For example, DART-MS presents unique opportunities in food and natural products chemistry, allowing for direct observation of the complex cascade of enzymatically induced flavor-releasing processes that rapidly occur when plants are cut [112], and monitoring the change of biochemical composition of tea during the fermentation and manufacturing process [113]. Besides, ESAI-MS has realized direct monitoring of chemical changes in the coffee bean during the roasting process, establishing a chemical fingerprint of the roast degree and its chemical markers [114]. And probe electrospray ionization mass spectrometry (PESI-MS) could be directly applied to analyze biological samples such as orange, banana, etc. [115].

3.1.3. Classification/authentication

AMS technologies are not only widely used in the analysis of regulated or functional compounds from food samples, but also have widespread application in classification/authentication of food samples. For instance, DART-MS allows for distinction between toxic Japanese star anise and non-toxic Chinese star anise fruits [116], and accurate prediction of the amounts of acrylamide formed during baking of biscuits samples based on fingerprinting and multivariate analysis [117]. Aiming at the retrospective control of feed fraud, DART-MS was also applied to profile the difference between the chicken meat based on slight differences in diet (feed with and without the addition of chicken bone meal) via the help of multivariate analysis of the acquired data sets [118]. In addition, with the linear discriminant analysis (LDA) model constructed with TAGs profiles, DART-MS has achieved animal fat (lard and beef tallow) authenticity assessment [119]. Also, DAPCI-MS could be used for identification authenticity of mutton [120], rapid differentiation of dried sea cucumber products [121], tea products [122], louts seeds freshness [123], propolis [124] as well as genuine ginseng [125], and high-throughput screening of sulfur fumigated Chinese star [126]. These results further showed that AMS techniques provided a practical and convenient tool for high throughput analysis of different real samples in food field, and could be developed as online direct technology used for fast discrimination/authentication.

The molecular fingerprinting of intact fruit samples combined with statistical data analysis can allow fast classification/authentication of food samples. For example, ND-EESI-MS was used for fast profiling of nonvolatile and semi-volatile compounds from various fruits, and different ripening stages of bananas, grapes, and strawberries are clearly differentiated via the help of principle of component analysis (PCA) [127]. Furthermore, ND-EESI-MS could be employed to differentiate the spinach contaminated by *Escherichia. coli* from normal green spinach and old spinach even without PCA, providing a practical and convenient method for on-line maturity monitoring of fruits and screening of contaminated vegetables [62]. And the method also could be utilized to differentiate frozen fish meat samples at different spoilage stages based on the biogenic amines known for microorganisms growing on meat (Fig. 6a) [62]. Similar to ND-EESI-MS, secondary electrospray ionization mass spectrometry (SESI-MS) was applied for preliminary study of grape ripening by rapid profiling mass spectra of volatile composition [128]. To identify alkaloids in lotus seeds and differentiate lotus seeds with different storage time, ethanol extracts of lotus seeds was clearly differentiated using EESI-MS with the help of PCA [129]. MPT-MS has achieved the direct assessment of navel quality and location of origin by combining molecular fingerprints with statistical data analysis (Fig. 6b) [130].

In addition, LESA-MS displayed excellent potential in meat species authentication [131,132], while rapid evaporative ionization mass spectrometry (REIMS) was found to be a promising tool in fast characterization of the meat products species of origin [133]. Also, EASI-MS permits group samples from similar plant origin and geographical origin [134], LTP-MS was utilized for rapid classification of coffee products based on data mining models [135], PS-MS was employed for chemical fingerprinting analysis for tracing origins and quality assessment of Bansha herbal tea [136], and SESI-MS achieved classification of artisanal cheddar cheeses [137]. All in all, above examples further showcased that AMS methodologies have played an important role in food safety and quality control. Table 2 shows the applications of AMS techniques in solid food samples.

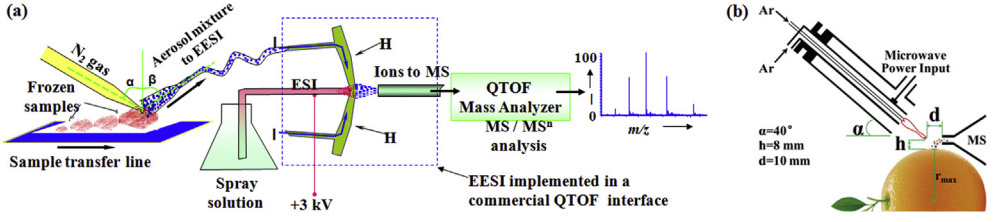

Fig. 6. Schematic diagrams of typical AMS techniques in solid foods analysis. (a) ND-EESI-MS for differentiation of frozen meat samples (reprinted from [62] with the permission of Wiley), and (b) MPT-MS for assessment of navel orange quality and location of origin (reprinted from [130] with the permission of ACS).

Table 2
The applications of AMS techniques in solid food samples.

Typical technologies	Food sample	Analytes	LOD[a]	RSD[b]	Ref[c].
DESI-MS	mango, passion fruit, papaya and strawberries	pesticides	33 pg/mm^2	below 20%	[78]
	fruit and vegetable	pesticides, insecticides, herbicides, fungicides	1–90 μg/kg	below 15%	[79]
	wheat	strobilurin fungicides	N/A[d]	8–15%	[83]
	chili powder tomato sauce sausage and fried egg	sudan dyes	0.01 pg/mm^2 0.02 pg/mm^2 0.02 pg/mm^2 1.0 pg/mm^2	N/A[d]	[98]
	cross-contaminated feed samples	veterinary drugs	lower 1μg/g	N/A[d]	[99]
	commercial small dog kibbles	omega-3 fatty acids	N/A[d]	N/A[d]	[109]
DART-MS	grapes, apples, and oranges	multiclass mixture of 132 pesticides	N/A[d]	N/A[d]	[80]
	fruit and vegetable	pesticides	N/A[d]	N/A[d]	[81]
	grapefruit	organophosphorous insecticide	N/A[d]	1.3–14%	[82]
	wheat and maize	mycotoxins	N/A[d]	2.2–16.5%	[94]
	maize	aflatoxin AFB1	N/A[d]	0.7–6.9%	[95]
	milk powder and milk products	melamine and cyanuric acid	170 and 450 μg/kg	5.3–7%	[100]
	fruit peels	fungicides, antioxidants, sugars	N/A[d]	6–14%	[104]
	Garlic, elephant garlic, leek, Chinese chives, and a commercial dietary supplement containing garlic powder	2-propenesulfenic 2-propenesulfinic acids, diallyl trisulfane s-oxide, and several reactive sulfur compounds and other alliums	N/A[d]	3.02%	[105]
	roasted ground coffee, instant coffee, and capsuled coffee	caffeine	N/A[d]	within 5%	[106]
	propolis	flavonoids and phenolic compounds	N/A[d]	N/A[d]	[107]
	soybeans	genistein, daidzein and glycitein	5 mg/kg	7–15%	[108]
	tea	biochemical composition	N/A[d]	N/A[d]	[113]
	star anise fruits	neurotoxic anisatin	<200 μg/kg	N/A[d]	[116]
	biscuits	acrylamide	3 μg/kg	N/A[d]	[117]
	chicken meat	metabolomic profile	N/A[d]	4.2–37%	[118]
	animal fat and their mixtures	Triacylglycerols and polar compounds	N/A[d]	4–16.9%	[119]
DAPCI-MS	milk products	pure melamine	3.4 × 10^{-15} g/mm^2	5.2–11.9%	[16]
	hot pot sauce materials	cocaine	1.5 × 10^{-12} g/mL	4.7–11.6%	[101]
	radish taproot	sinapine	10^{-12}–10^{-7} g /cm^2	5–8%	[103]
	duck, beef, pork, beef, mutton and mutton-flavored fake meat sample	characteristic chemicals	N/A[d]	N/A[d]	[120]
	sea cucumber products	characteristic chemicals	N/A[d]	N/A[d]	[121]
	tea products	characteristic chemicals	N/A[d]	N/A[d]	[122]
	louts seeds	characteristic chemicals	N/A[d]	N/A[d]	[123]
	propoils	characteristic chemicals	N/A[d]	N/A[d]	[124]
	genuine ginseng	ginsenosides	N/A[d]	N/A[d]	[125]
	sulfur fumigated chinese star	characteristic chemicals	N/A[d]	N/A[d]	[126]
	pet foods	melamine	3.05 μg/kg	7.4–9.5%	[138]
LTP-MS	fruits and vegetable	multi-class agricultural chemicals	0.5 μg/L	N/A[d]	[89]
	coffee products	caffeine and purines	N/A[d]	N/A[d]	[135]
LC/DBDI-MS	apples and baby food	pesticides	10 pg/mL	3.9–21.2%	[84]
	apple, orange and tomato	43 pesticides	N/A[d]	2.2–17.3%	[85]
PS-MS	fruits and vegetables	pesticides	below 5 mg/kg	N/A[d]	[86]
	arugula, basil, cabbage, lettuce and kale	atrazine, diuron and methomyl	1.23–25.00 ppb	N/A[d]	[87]
	beef	clenbuterol	1 ng/g	N/A[d]	[102]
	Bansha herbal tea	chemical fingerprint	N/A[d]	6.3–9.6%	[136]
LS-MS	arugula, basil, cabbage, lettuce and kale	atrazine, diuron and methomyl	0.03–36.00 ppb	N/A[d]	[87]
LESA-MS	raw and cooked meat	peptides	N/A[d]	N/A[d]	[131]
	processed meat products	peptide markers	N/A[d]	N/A[d]	[132]
MFGDP-MS	foodstuffs	ametryn, amitraz, buprofezin, etc.	0.13 ng/g mm^{-2}	3.5–13.5 %	[90]
TD-ESI-MS	fruits and vegetables	pesticides	0.5 μg/L	below 14%	[91]
ND-EESI-MS	spinach	metabolites	10 fg/cm^2	7.2%	[62]
	frozen fish meat	biogenic amines	N/A[d]	N/A[d]	[63]
	bananas, grapes, and strawberries	nonvolatile and semi-volatile compounds	N/A[d]	N/A[d]	[127]
MPT-MS	juice sac and exocarp of navel oranges	vanillin	0.119 μg/L	1.7%	[130]
EESI-MS	Louts seeds	alkaloids	N/A[d]	N/A[d]	[129]
ESSI-MS	fruits	oligosaccharides, alpha hydroxyacids	N/A[d]	N/A[d]	[110]
PESI-MS	orange, banana	characteristic compounds	N/A[d]	N/A[d]	[115]
EASI-MS	meats and fats	triacylglycerols	N/A[d]	N/A[d]	[111]
	coffee bean	chemical markers	N/A[d]	N/A[d]	[114]
	propolis	chemical fingerprinting	N/A[d]	N/A[d]	[134]
REIMS	meat products	fatty acids, glicerophospholipids	N/A[d]	N/A[d]	[133]
DEP-MS	groundnuts, wheat and maize	aflatoxin B1	0.8 ppb	N/A[d]	[96]
SESI-MS	grape	volatiles	N/A[d]	N/A[d]	[128]
	artisanal cheddar cheese	volatile compounds	N/A[d]	N/A[d]	[137]

N/A[d] represents information not available.
[a] LOD represents the low of detection.
[b] RSD represents relative standard deviations.
[c] Ref represents references.

3.2. Liquid foods

Above section, the application of AMS in solid foods was described. In this part, we mainly focuse on the application of AMS in liquid food samples, including (1) milk and dairy products, (2) nonalcoholic beverages, and (3) alcoholic beverages.

3.2.1. Milk and dairy products

Milk is nature's perfect food, while dairy products are considered to be nutritious foods, both of them are very popular among the public [139]. Hence direct detection of harmful contaminants such as melamine in various milk and dairy products increasingly gains the attention from society since the milk scandal in 2008 [140]. Researches validated that AMS techniques have extensive applications in food science, which can significantly improve our life quality [141]. For example, EESI-MS is useful for screening of trace melamine in raw milk and extracts of wheat gluten and milk powder [142]. Similarly, nanoEESI-MS has obtained direct analysis of melamine in raw milk [60]. Furthermore, a novel molecular imprinting technology integrated with membrane electrospray ionization mass spectrometry (MESI-MS) has showed excellent performance for direct analysis of ciprofloxacin (CPFX) in fresh milk, with a low quantification limits of 1 ng/mL [143]. Solid-phase extraction based on magnetic molecularly imprinted polymers (MMIP-SPE) coupled with iEESI-MS was designed for the quantitative analysis of trace fluoroquinolones in raw milk samples (Fig. 7a), the established method showed LOD was lower than 0.03 μg/L and a high analysis speed (≤4 min per sample) [144].

Based on good analysis performances, AMS techniques could be used for direct detection of antibiotic compounds. For instance, LDTD-APCI-MS/MS obtained quantitation of seven sulfonamides residues in dairy milk, the limits of quantitation of them were 2–14 μg/L [65]. DART-MS achieved quantitative determination of aflatoxin M1 [145] and high-throughput screening of antiparasitic veterinary drugs such as benzimidazolic compounds in milk [146]. Solid-phase microextraction-transmission mode (SPME-TM) in conjunction with DART-MS also obtained fast screening and quantitation of pesticides in of cow milk (Fig. 7b) [147]. Additionally, characterization of major chemical components on dried milk with different fat contents was achieved by using ELDI-MS [148].

3.2.2. Nonalcoholic beverages

Lead is toxic to human beings beyond a certain exposure level, consequently, direct and rapid analysis of trace lead in complex liquid foods is important. As one of the typical AMS ionization techniques available for liquid foods analysis, EESI-MS provides a scientific tool at the molecular level to detect trace lead in various drinks including mineral water, energy drinks, soft drinks, orange juice, and tea, the LOD of EESI-MS for lead was 10^{-13} g/mL [149]. Similarly, nanoEESI-MS has been applied for direct analysis of functional ingredients including vitamins, taurine, lysine, inositol, nicotinamide and caffeine vitamin B_6 in Red Bull energy drink, Coco-cola, and Pepsi samples [60], and sensitive quantitative detection of cocaine in beverages [150]. Besides, SPME-TM-DART-MS achieved quick screening and quantitation of multiresidue pesticides in grape juice and orange juice [147], and direct analysis of molecules in fruit juice of apple, pear and watermelon were performed using PS-MS [151]. Based on nanoliter-level sampling technique, DAPCI-MS has been developed for determination of trace dimethoate in juices, the LOD of dimethoate was determined to be 1.2×10^{-11} mg/kg [152]. Electrostatic spray ionization mass spectrometry (ESTASI-MS) has realized quantitative determination of caffeine in different beverages, and the result is in good agreement with that obtained by the classical standard addition method [153]. Under simultaneous multiple reaction monitoring (MRM) model, 4-methylimidazole [154] and caffeine [155] in commercial beverages were directly analyzed by PS-MS, which greatly extends the scope of AMS for *in situ* analysis of liquid foods.

3.2.3. Alcoholic beverages

Alcoholic beverages play an important role in people's daily life, but driven by high profit, some illegal traders often use inferior liquors instead of the products with high quality [156]. Based on excellent performance in sensitivity and high-throughput, AMS techniques provided reliable support to ensure public access to good quality liquors. For instance, ambient glow discharge ionization mass spectrometry (APGDI-MS) was applied to differentiate different brands of Chinese liquors [156]. Desorption nano-electrospray ionization mass spectrometry (nano-DESI-MS) profiled anthocyanins in wine and wine mixtures, providing a new scientific tool to uncover adulteration of

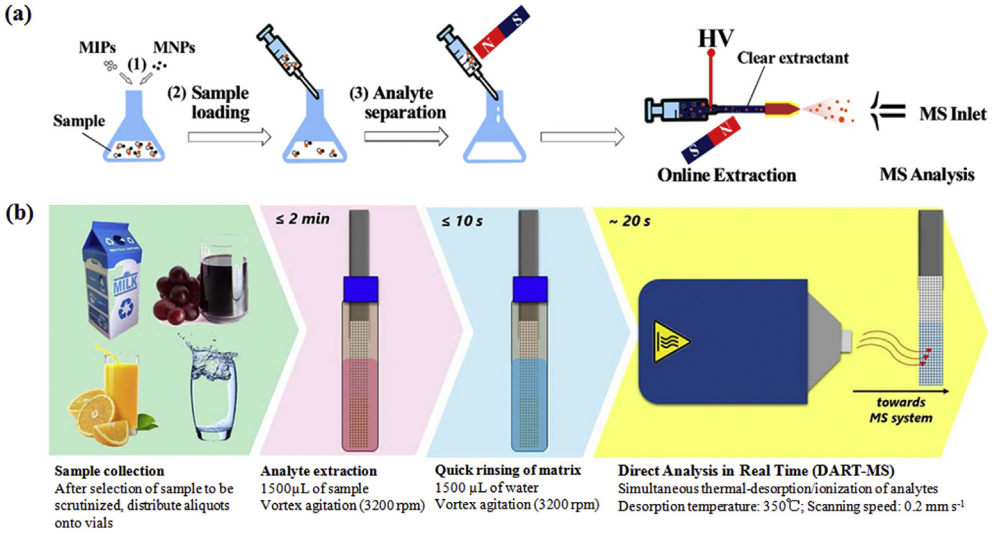

Fig. 7. Schematic illustrations of AMS methods in liquid food samples analysis. (a) MMIPs-SPE-iEESI-MS for quantification of fluoroquinolones in milk (reprinted from [144] with the permission of Springer Nature), and (b) the analytical workflow of SPME-TM-DART-MS for the ultrafast determination of pesticides in food matrices (reprinted from [147] with the permission of ACS).

wine by detecting the unnatural or unusually high amount of anthocyanins [157]. DART-MS was developed for direct analysis of multiple mycotoxins in beer [158], and showed satisfactory performance for beer origin recognition and quality monitoring/authenticity assessment [159]. Additionally, air-flow-assisted extractive electrospray ionization mass spectrometry (AFAI-EESI-MS) was established for direct analysis of phthalic acid esters in spirits, the LODs were measured to be 0.011–0.035 μg/g [160], while quantification of coumarin in woodruff-flavored liquor was carried out using DIP-APCI-MS [161].

Of course, AMS methods can also be used for analysis of allergens in liquid food sample. For example, lysozyme, as one of the most important food allergens in white wine samples, was rapidly detected by EESI-MS. The LOD for chicken egg lysozyme in white wine sample was 5 μg/mL, which was lower than the amounts that can provoke allergic reactions (oral test with 3 mg or labial test with 1 mg/mL) [162]. Besides, EESI-MS has acquired simultaneous sampling of volatile and non-volatile analytes in beer, which further extends the application of AMS technologies in analysis of complex liquid sample with high gas content like beer [163]. Similarly, coupled with standard addition method, rapid quantitative detection of histamine in beer was achieved by nanoEESI-MS, the LOD of this method for histamine was 0.02 μg/mL [164]. Based on PS-MS and MRM, a quantitative method for the assay of resveratrol in red wines was developed [165]. Moreover, rapid qualitative and semi-quantitative determination of multiclass fungicides in wines has been validated by LTP-MS, which indicated that the method could be further extended towards the detection of other analogous chemicals such as dyes, sweeteners and preservatives, not only in wines but various beverages [166]. Table 3 shows the applications of AMS techniques in liquid food samples.

3.3. Viscous foods

Viscous samples are common in daily life and also play a significant role in research laboratories, food science and industries [64], but fast analysis of viscous samples at molecular level remained a challenge for the analytical science. Owing to some AMS techniques could real-time and online obtain chemical information of highly viscous samples. Until now, they have been successfully applied for rapid characterization of regulated and functional compounds as well as classification and quality assessment of viscous food samples.

3.3.1. Detection of regulated compounds in honey

Chemical pollutants have been important factors affecting the quality of bee products [167], therefore, the establishment of reliable platform to detect trace chemical residues in highly viscous samples like honey at the molecular level is very important. With high sensitivity and precision, ND-EESI-MS has achieved direct quantitative analysis of tetracycline and dichlorvos in honey, the result showed the LOD for etracycline and dichlorvos was 1.08 ng/mL and 1.0 ng/mL, respectively [168,169]. Besides, both ND-EESI-MS and LDTD-APCI-MS/MS has obtained quantitative analysis of chloramphenicol (CAP) in honey, the LOD of LDTD-APCI-MS/MS and ND-EESI-MS for CAP in honey was 0.19 ng/g [170] and 0.3 ng/mL, respectively [167]. These examples further proved that AMS methods could provide useful reference for the detection of other antibiotic/pesticides residues in honey.

3.3.2. Direct analysis of oils

Oil, a product with high nutritional value and significant health benefits, is one of representative and necessary viscous samples in public daily life. Usually, TAG and free fatty acids (FFA) are the main

Table 3
The applications of AMS techniques in liquid food samples.

Typical technologies	Food sample	Analytes	LOD[a]	RSD[b]	Ref.[c]
EESI-MS	raw milk, extracts of wheat gluten and milk powder	melamine	200–500 ppb	N/A[d]	[142]
	mineral water, lake water, tap water, energy drinks, soft drinks, beer, orange juice, and tea	lead	10^{-13} g/ml	4.6–7.6%	[149]
	white wine	lysozyme	5 μg/mL	8.0–15%	[162]
	beer	volatile and non-volatile analytes	N/A[d]	N/A[d]	[163]
nanoEESI-MS	milk/Red Bull beverage	melamine/taurine, lysine, inositol, nicotinamide and caffeine vitamin B_6	11 pg/ml	5–10%	[60]
	Red Bull energy drink, Coco-cola, and Pepsi samples	cocaine	7–15 fg	6.9–8.6%	[150]
	beer	histamine	0.02 μg/ml	5–11%	[164]
nanoDESI-MS	wine, wine mixtures and berries	anthocyanins	N/A[d]	N/A[d]	[157]
DART-MS	milk	aflatoxin M1	N/A[d]	9.6–13.5%	[145]
	milk	benzimidazolic compounds	1 μg/kg	below 10%	[146]
	beer	multiple mycotoxins	N/A[d]	11–28%	[158]
MESI-MS	milk	ciprofloxacin	N/A[d]	N/A[d]	[143]
MMIP-SPE-iEESI-MS	milk	fluoroquinplones	≤0.03 μg /L	below 10.9%	[144]
LDTD-APCI-MS/MS	dairy milk	seven sulfonamides residues	2–14 μg /L	below 10%	[65]
ELDI-MS	dried milk	major chemical components	N/A[d]	N/A[d]	[148]
DAPCI-MS	juices	dimethoate	1.2×10^{-11} mg/kg	8.4–26.9%	[152]
LTP-MS	wine	multiclass fungicides	below 50 pg	5–25%	[166]
PS-MS	juices of apple, pear and watermelon	oligosaccharides	0.8 mg/L	below 9%	[151]
	commercial beverages	4-methylimidazole	5 pg/μL	2–10%	[154]
	beverages	caffeine	1.6 μg/mL	below 13%	[155]
	red wine	resveratrol	0.5 μg/mL	below 7%	[165]
APGDI-MS	Chinese liquors	volatile components	N/A[d]	N/A[d]	[156]
ESTASI-MS	beverages	caffeine	10 ng/ml	N/A[d]	[153]
AFAI-EESI-MS	spirits	Phthalic acid esters	0.011–0.035 μg/g	N/A[d]	[160]
DIP-APCI-MS	woodruff-flavored liquor	coumarin	7.2 mg/kg	0.9–12.6%	[161]

N/A[d] represents information not available.
[a] LOD represents the low of detection.
[b] RSD represents relative standard deviations.
[c] Ref represents references.

components of oil, but a series of minor polar compounds are also present. Nevertheless, owing to highly complex matrices and adulteration, it's urgent to develop preferable methods that are rapid, straightforward and accurate to evaluate oil quality [3]. Currently, numerous AMS techniques have been developed for oil sample analysis. For example, LTP-MS acquired detection of chemical compounds including free acids, phenolics and volatiles in raw olive oil [171]. DESI-MS measured FFA from various oil samples [172], and directly analyzed triglyceride composition and oxidation behavior of edible oils and margarine samples [173]. EASI-MS has been used for qualitative and quantitative analysis of TAG and FFA as well as other bioactive constituents from various oils [174–178], quality control of valuable Andiroba oil [179] and Brazil nut oil [67], and certification of geographical origins of olive oil [180]. Also, EASI-MS was utilized to follow the maturation of Jatropha curcas L. seeds via monitoring the TAG profile of the oil samples, the results showed that TAG composition is significantly modified during seed development but remains nearly unchanged during storage [181]. Besides, microjet sampling in combination with EESI-MS was applied to rapid characterization and classification of extra virgin olive oil [182]. DAPCI-MS has obtained screening of inferior quality oils [183], and analysis of edible oil based on back propagation neural networks [58]. DART-MS could be employed for olive oil quality and authenticity assessment [184], while ND-DBDI-MS has accomplished fast and accurate identification of hogwash oil from qualified edible oil samples with the help of PCA [66].

3.3.3. Others viscous foods

Apart from wide applications of AMS techniques in honey and oil, they could also be used for others viscous food samples analysis. As a demonstration, ND-EESI-MS recorded the mass spectral data about volatile and nonvolatile analytes on greasy cheese surface, suggesting that the established method is of capability for sensitive detection analytes on greasy surfaces without chemical contamination [185]. DAPCI-MS obtained direct detection of cocaine in mashed potato [186] and trace typical food additives including sudan I, sudan II, sudan III and sudan IV in tomato sauce [187]. With no chemical contamination and high voltage damage to the analytes, TDCI-MS has been developed for rapid detection of trace pesticide residues such as dimethoate in highly viscous fruit juice samples [188]. Overall, above results further confirmed that AMS techniques are amenable to characterization, classification and authentication of viscous foods in food science, showing promising applications for online quality monitoring in the area of food safety. Table 4 shows the applications of AMS techniques in viscous food samples.

3.4. Bulk foods

Of course, apart from analysis of solid, liquid and viscous food samples, rapidly revealing the chemical information inside bulk foods is of significant importance for food science and industry. Owing to requiring no mashing/grinding the sample or matrix clean-up, internal chemical information of bulk sample can been directly obtained at molecular level by iEESI-MS. Until now, iEESI-MS has been widely applied to the qualitative and quantitative analysis of bulk food samples (e.g., fruits, vegetables, and meat species) from plant/animal origin food samples, opening new possibilities in food science and industry.

3.4.1. Bulk food samples of plant origin

For instance, iEESI-MS was used for rapid differential analysis of strawberry maturity [26], evaluation quality of navel oranges from different habitats [191], direct characterization of chemical composition in asparagus [192] and avocado [193]. Similarly, iEESI-MS could be applied for direct characterization of nutrient components including choline, fructose and sucrose in red peppers with different freshness, and decline curves correlated to the metabolism of red pepper were plotted, which not only allowed the freshness and quality of red pepper to be differentiated at

Table 4
The applications of AMS techniques in viscous food samples.

Typical technologies	Food sample	Analytes	LOD[a]	RSD[b]	Ref.[c]
ND-EESI-MS	honey	chloramphenicol	0.3 ng/mL	5.96–8.82%	[167]
		etracycline	1.08 ng/ml	1.12–3.28%	[168]
		dichlorvos	1.0 ng/mL	below 4.4%	[169]
	greasy cheese	volatile and nonvolatile analytes	N/A[d]	N/A[d]	[185]
LDTD-APCI-MS/MS	honey	chloramphenicol	0.19 ng/g	8–24%	[170]
EESI-MS	extra virgin olive oil	E-2-hexenal, trans-trans-2,4-heptadienal, tyrosol and caffeic acid	N/A[d]	N/A[d]	[182]
DESI-MS	olive oil, fish oil	fatty acids	2–10 μg/L	6%	[172]
	edible oils and margarine samples	triglyceride	N/A[d]	N/A[d]	[189]
DART-MS	olive oil	triacylglycerols and/or polar compounds	N/A[d]	N/A[d]	[184]
DAPCI-MS	edible oil	characteristic chemicals	N/A[d]	3.5–15%	[183]
	mashed potato	cocaine	N/A[d]	N/A[d]	[186]
	tomato sauce	sudan I, sudan II, sudan III and sudan IV	N/A[d]	N/A[d]	[187]
	edible oil	characteristic chemicals	N/A[d]	7.2%	[190]
LTP-MS	raw olive oil	free acids, phenolics and volatiles	N/A[d]	N/A[d]	[171]
TDCI-MS	highly viscous fruit juice	dimethoate	8.76×10^{-11} gml^{-1}	3.1–10.0%	[188]
ESAI-MS	Brazil nut oil	TAG	N/A[d]	N/A[d]	[67]
	vegetable oils	TAG and FFA	N/A[d]	N/A[d]	[174]
	vegetable oils	TAG	N/A[d]	N/A[d]	[175]
	oils from different seeds	TAG, FFA, natural acids and phenolic constituents	N/A[d]	N/A[d]	[176]
	Amazonian vegetable oils	TAG, FFA, phytosterols and limonoids	N/A[d]	N/A[d]	[177]
	chia oil	TAG	N/A[d]	N/A[d]	[178]
	the Andiroba oil	TAG, FFA and limonoid	N/A[d]	N/A[d]	[179]
	olive oil	FFA and phenolic constituents	N/A[d]	N/A[d]	[180]
ND-DBDI-MS	hogwash oil and edible oil samples	FFA	N/A[d]	1.9–12.5%	[66]

N/A[d] represents information not available.
[a] LOD represents the low of detection.
[b] RSD represents relative standard deviations.
[c] Ref represents references.

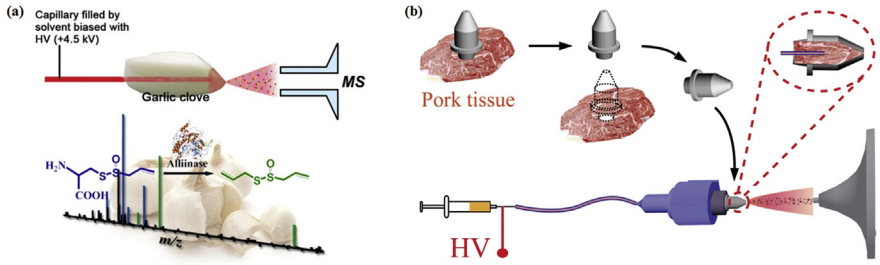

Fig. 8. Schematic illustrations of iEESI-MS for bulk sample analysis. (a) molecular characterization of ongoing enzymatic reactions in raw garlic cloves (reprinted from [25] with the permission of ACS), and (b) direct quantitative analysis of 6 β-agonists in bulk pork tissue sample (reprinted from [70] with the permission of ACS).

molecular level, but also showed valuable reference for freshness evaluation of other vegetables and fruits [194]. Besides, iEESI-MS allowed rapid recognition of metabolic changes in the garlic tissue subjected to various external stimuli [195]. Direct and molecular characterization of ongoing enzymatic reactions occurring in raw biological samples is of increasing interest, iEESI-MS has successfully followed the chemical conversion of alliin to allicin, catalyzed by allinase, in garlic cloves (Fig. 8a) [25]. These results further demonstrated that iEESI-MS plays a paramount role in direct characterization of nutrients and phytochemicals in various bulk food samples of plant origin.

3.4.2. *Bulk food samples of animal origin*

Animal origin food is an important category of human daily diet. Owing to the abuse of veterinary drugs like β-agonists can pose potential hazards to public health, with serious symptoms such as muscular tremors, cardiac palpitations, headaches, and muscular pain, even causing life threatening, cardiovascular and central nervous disease [196,197], hence the efficient tools beneficial for the analysis of trace β-agonists from numerous animal-derived food samples is indispensable. iEESI-MS was employed to analyze different samples, including lean pork, fat pork, pig lung, beef, ham sausage, pig heart, smoked pig feet, and bacon, the results indicated that iEESI-MS method is available for direct detection of trace clenbuterol and procaterol embedded in meat samples [198]. Besides, accurate iEESI-MS quantitative analysis of 6 β-agonists in bulk pork samples showed good performance, which further extends the quantification potential of AMS techniques for the molecules at the surface of solid samples (e.g., in μg/cm^2 units) toward the molecules inside bulk sample volume (i.e., in μg/kg units) (Fig. 8b) [70]. Combining PCA with correlation analysis, iEESI-MS was used for direct investigation of metabolic effects of clenbuterol and salbutamol on pork quality at the molecular level [199]. Also, iEESI-MS combined graphene oxide particles functionalized with amylopectin to selectively adsorb hemoglobin present in the blood (e.g. chicken, duck, sheep, mouse, pigeon, and turtledove) and meat juice samples, realizing rapid identification of meat species based on the difference in molecular composition of hemoglobin reflected in MS [200].

3.5. *Food imaging*

MSI offers great advantages to explore the spatial-chemical information from food samples [201], and has emerged as a powerful technique for food safety and quality through monitoring 3-D spatial distribution of nutrients that determines food quality [202]. Despite many foods imaging examples were reported with techniques like MLDAI-MS [203–205], it's beyond discussion scope of this section. Here, the current status of food imaging with AMS techniques is mainly reviewed.

Generally, knowledge about the spatial distribution of metabolites in a given food sample might lead to novel findings in food science. For example, distribution of endogenous melamine in a boiled chicken egg was imaged with DAPCI-MS, the chemical image (Fig. 9a) evidently revealed that melamine was mostly located in the egg white rather than egg yolk, and this was attributed to the strong hydrogen bonding between melamine and proteins in the egg white [206,207]. LTP-MSI images clearly revealed the non-uniform distribution of several metabolites in a cross-cut of Jalapeño chili (*Capsicum annuum*) (Fig. 9b), laying the solid base of LTP-MSI for the discovery of known and unknown volatile and semi-volatile metabolites in others food samples [208]. Also, imaging analysis of *m/z* 357, deprotonated *malabaricone C*, in a blotted Myristica malabarica seed was acquired by DESI-MS, which obviously showed the distribution information of the compounds in the seed substructures [209]. Besides, the spatial distribution of chlorogenic acids and sucrose across coffee bean endosperm was obviously revealed by DESI-MS imaging, and the result was favorable to expand knowledge about coffee chemistry and physiology [210]. Moreover, the distribution of antioxidant tocopherol, a compound with vitamin E activity and common food additive, in a sage leaf was imaged with DAPPI-MS [211]. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) imaging obtained the elemental distribution in peanut seed [212], the developing wheat grain [213], and the cross-section of a brown rice grain [214]. In brief, these results further demonstrated that MSI techniques could be performed *in situ*, real-time to obtain the distribution information of special molecules on the surface of food samples and even on the level of cell/subcellular.

4. Conclusions and prospects

Conclusively, with the rapid developments of AMS methods, the extensive array of newly developed AMS techniques improve throughput, simplicity and operational cost of food sample analysis, and allow online and real-time analysis of samples in their native conditions and under ambient atmosphere. They have become a versatile tool for food safety and quality in food science and industry, providing reliable certification support for food legislation to some extent. However, during practical application, most technologies still need take the sample back to the laboratory for analysis, this is attributed to the limitations of the technology itself and mass spectrometer. For example, some AMS technologies require sheath gas, while some mass spectrometers are usually with big size. In terms of above-mentioned common AMS methods, methanol and other toxic chemical regnant are required in DESI-MS to produce primary ions, resulting in food contamination and even the analyzed qualified sample might be unsuitable for direct use. Unlike DESI-MS, DAPCI-MS, LTP-MS, and APGDDI-MS, etc. through corona discharge to produce primary ions, without any toxic or harmful reagents

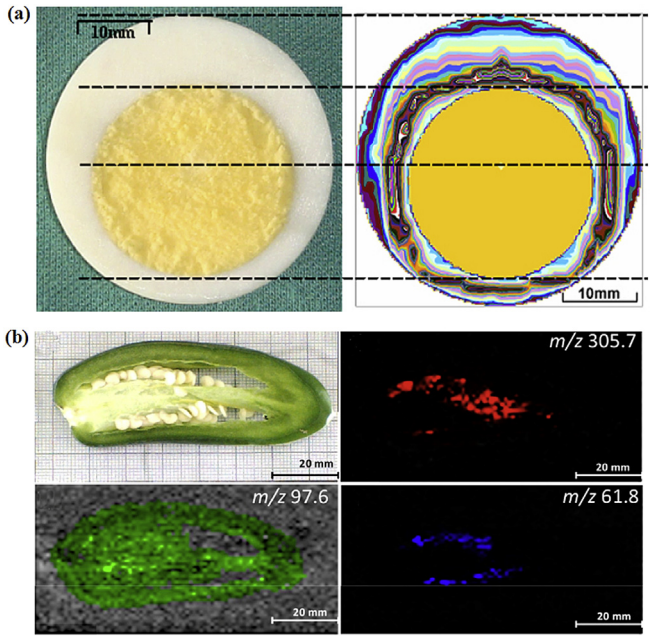

Fig. 9. The application examples of food imaging. (a) Optical image of melamine in egg samples by DAPCI-MS (reprinted from [206] with the permission of Elsevier), and (b) LTP-MSI of a cross-cut of a Jalapeño chili (*Capsicum annuum*) fruit (reprinted from [208] with the permission of Elsevier).

were used, so there will be no chemical contamination for the analyzed food sample. From this regard, these techniques can be applied for remote, online monitor of food samples. For ND-EESI-MS, the sampling and ionization process were totally separated from both space and time, allowing profile of different type of food samples such as vegetables, fruit, frozen meat and honey etc. by a gentle stream of air or gas. Without chemical pollution and damage, it can also be applicable for online and remote analysis under extreme conditions such as low/high temperature and dangerous environment. Particularly, ND-EESI-MS exerts evident advantages in viscous food samples analysis. Also, iEESI-MS could be employed to rapid qualitative and quantitative analysis of endogenous and exogenous chemical components in various bulk food samples, opening new possibilities for food science and industry. Moreover, MSI techniques further delivered detailed understanding of compounds within various food samples on different length scales, from surface to cell and even subcellular level.

However, owing to food sample diversity, highly complex matrices, and trace analyte concentration, AMS is facing a great challenge about accurate quantification of known and unknown targeted analytes inside different food matrices and operation standardization. To make AMS techniques more analytically useful, these aspects, including sample introduction, reproducibility, sensitivity, selectivity, matrix effects, linearity, precision, accuracy and method validation, must be carefully and fully addressed. Despite AMS reduces the analysis time compared with LC-MS, which obtained at the cost of lower sensitivity, and matrix effects during the process of desorption and ionization also can cause lower sensitivity. To improve the sensitivity of AMS, computer modeling of ions sampling/transport and MS interface/ion optics are considered as valuable tools that should be applied more in the future [215,216]. Usually, the reproducibility and inter-laboratory repeatability of AMS analysis might be inconsistent owing to environmental conditions, sample geometry and makeup, and even user operation or platform configuration differences [217]. Consequently, the establishment of universal and inclusive databases of AMS regardless of ionization techniques, mass spectrometers and conditions of MS analysis, which would be of significance for rapid screening of trace toxic compounds and evaluation of the food quality [218]. Moreover, noted that complex spectra (as encountered with all direct MS techniques) require the help of chemometric tools for data evaluation [219], hence advancements in automation and machine learning will offer valuable avenues for ongoing and in-depth research of AMS in food science [217].

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