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Tip-assisted ambient electric arc ionization mass spectrometry for rapid detection of trace organophosphorus pesticides in strawberry

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ABSTRACT

In this study, an ambient mass spectrometry (AMS) based method was developed for rapid detection of organophosphorus pesticides in strawberry. This method combines an electric arc and a microsyringe tip to realize tip-assisted ambient electric arc ionization (TAAEAI). A high-voltage electric arc can be applied to the microsyringe tip to generate an electric field, which results in corona discharge at the microsyringe tip. The juiced strawberry sample loaded on the tip could be directly ionized with TAAEAI and then analyzed by a mass spectrometer. TAAEAI-MS was successfully applied to analyze 6 organophosphorus pesticides in three strawberry samples. Malathion and profenofos were detected from the investigated strawberry samples. This method could quantitatively determine the contents of organophosphorus pesticides in strawberry with high reproducibility, high precision, and high sensitivity. Sample matrices did not interfere with the pesticide analysis. The recoveries of organophosphorus pesticides spiked in strawberry samples varied between 82.6% and 116% with relative standard deviations (RSDs) less than 9.2%. The limits of detection (LODs) varied between 0.0124 μg/g and 0.0245 μg/g, while the limits of quantification (LOQs) varied between 0.0413 μg/g and 0.0817 μg/g. The coefficients of determination (R^2) of the method were determined to be >0.995. The method established here may have potential application in the detection of organophosphorus pesticides in vegetables and fruits.

Vegetables and fruits are rich in carbohydrates and vitamins. Recent years have witnessed an increasing consumption of these two essential foods [1–3]. However, pests and diseases frequently impact their yields [4]. Therefore, a variety of pesticides are often used to control pests and weeds in the fields [5]. However, pesticides cause serious damage to ecological system and seriously affect human health once entering the body [6–8]. Many evidences have indicated that some severe diseases such as cancer and leukemia are closely related to pesticides [9–12].

Strawberry is a popular fruit and often used as a significant ingredient in food manufacturing because of its unique fragrance and excellent taste [13,14]. Studies have shown that hot and humid environment, such as in the plastic greenhouse, easily causes fungi growth and crop diseases. Unfortunately, strawberry in most parts of China grows in such an unfavorable environment [15–17], and varieties of pesticides are used in a large amount during the cultivation of strawberry, resulting in far higher concentrations of pesticide residues in strawberry than in other fruits. Therefore, the analysis of pesticides in strawberry has recently become a hot research topic. It is worth noting that organophosphorus pesticides have a bulk of applications in crop planting due to their strong and broad-spectrum insecticidal efficacy [18–20]. Organophosphorus pesticides can be distributed quickly to various organs and tissues once entering the human body. They inhibit the activity of acetylcholinesterase and thus prevent acetylcholine from being hydrolyzed, causing poisoning and even death [21–23].

Mass spectrometry (MS) is generally used to detect pesticides in foods following liquid chromatography separation [24–28], and provides reliable analysis with great detection performance. Ambient mass spectrometry (AMS) techniques allow direct analysis of compounds in raw food samples with minimal or no sample pretreatment. Desorption electrospray ionization MS (DESI-MS) and direct analysis in real time MS (DART-MS) are the first developed

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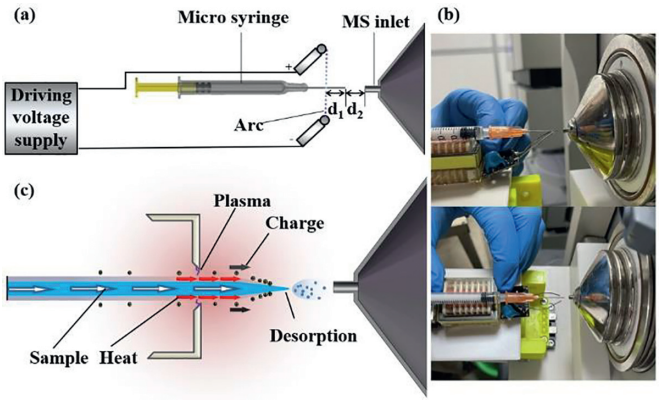

Fig. 1. The schematic diagram (a), photos (b), and ionization mechanism diagram (c) of TAAEAI-MS setup. d_1 is the distance between the needle tip and the arc, and d_2 is the distance between the needle tip and MS inlet.

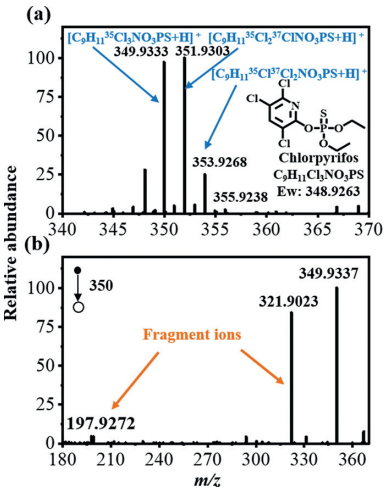

Fig. 2. The MS (a) and MS/MS (b) spectra of chlorpyrifos (10 μg/g) recorded by TAAEAI-MS. The error is within the tolerance range of 10 ppm.

AMS techniques. Paper spray ionization MS (PSI-MS) and dielectric barrier discharge ionization MS (DBDI-MS) are subsequently developed to detect and analyze pesticides [29–32]. In addition, since the tip has a charge accumulation effect, metal tips are often used in AMS techniques to assist ionization, whose mechanism is similar to atmospheric pressure chemical ionization (APCI) [33–35]. However, most AMS techniques are still subject to complex sample matrices, long sample pretreatment and detection times.

Electric arc based MS is a new AMS technique developed in 2020. Arc plasma dissociation MS (APD-MS) was used to detect fingerprint under atmospheric condition [36]. High energy and voltage of APD can desorb and ionize target molecules. Then, the team used APD to split and ionize the polymer, and obtained the structural information of the polymer through fingerprint analysis [37]. Ambient electric arc ionization MS (AEAI-MS) with a soft ionization source is a novel, versatile AMS technique to analyze compounds with a wide range of polarities [38]. Notably, AEAI only requires an open arc for ionization without laser and gas input. AEAI realizes the analysis of samples in solid, semi-solid, liquid, and gaseous states, and has good salt and matrix tolerances [39]. Besides, a portable MS ionization source named "MasSpec Pointer" with a mass of only 65 g was recently developed and used for the positioning of fatty acid carbon-carbon double bonds and the rapid detection of pesticides [40].

In this study, we built a tip-assisted ambient electric arc ionization (TAAEAI) device, and developed a detection method combining TAAEAI and high-resolution orbitrap MS for simultaneous analysis of 6 organophosphorus pesticides in strawberry. The accuracy, precision, limits of detection (LODs), and limits of quantification (LOQs) of the method met the requirements of pesticide residue analysis. The results showed that TAAEAI-MS is suitable for simultaneous detection of multiple pesticides in vegetables and fruits.

As shown in Fig. 1, the needle of a microsyringe containing a proper amount of liquid sample is placed on the arc discharge region. The arc is 1–5 mm away from the needle tip. When the liquid sample is pushed out, the arc plasma not only has enough temperature to desorb the sample, but also generates a discharge region in the surrounding air. The gas-phase analyte can be attached with the active charged particles in the arc plasma (mainly protonated water cluster ions) and then enter the mass spectrometer to be detected. The presence of the metal tip can greatly improve the ionization efficiency of the sample. On the one hand, the metal needle tube can transfer the heat generated by the arc to the sample and help the sample thermally desorb. On the other hand, the arc can be regarded as a charge generator, which can continuously provide free charges to the metal needle tube. The needle tip can accumulate charges due to its sharp shape, which is beneficial to increase the ionization efficiency. The whole analysis takes only a few seconds from sampling to data collection.

Parameters of d_1, d_2, and arc voltage were optimized for best ionization. We used malathion at a concentration of 10 μg/g as model molecule. The peak intensity-distance curves/arc voltage are shown in Fig. S1 (Supporting information). The optimal d_1 was 3 mm with highest peak intensity observed. When d_1 was less than 3 mm, the arc was too close to the needle tip, and would burn and destroy the sample. Meanwhile, large d_1 (>3 mm) was not conducive to heat transfer and arc ionization. The optimal d_2 was 3 mm, too. When d_2 was set at 1–3 mm, the peak intensity of $[\text{malathion}+\text{H}]^+$ was pretty high. When d_2 was more than 3 mm, the peak intensity significantly reduced. Given that short d_2 (<3 mm) would trigger the analyte being more easily sucked in the MS inlet by negative pressure, the optimal d_2 was thus set at 3 mm. In addition, we determined the optimal arc voltage as 7 kV (Fig. S1c), which was consistent with previous work. All the subsequent experiments were performed under the optimal conditions.

Commercial strawberry juice samples spiked by 6 pesticides at the concentration of 10 μg/g were used to test the TAAEAI-MS method. Fig. 2a and Fig. S2 (Supporting information) showed that the protonated ions of pesticides could be successfully detected with low interference by sample matrix. Therefore, the protonated pesticide ions were chosen for subsequent qualitative and quantitative analysis. Collision-induced dissociation (CID) was also performed to fragment the target ions of pesticide-spiked strawberry juice samples (Fig. 2b and Fig. S3 in Supporting information). The literature-supported fragmentation pathways of precursor ions are shown in Fig. S4 (Supporting information) [41]. These results indicated that TAAEAI-MS could effectively analyze pesticides in the samples containing complex matrices.

We next used commercial strawberry juice samples spiked by 6 pesticides to establish a quantitative TAAEAI-MS method. A series of strawberry juice samples containing mixed pesticide standard solutions were made and the calibration curves were established (Fig. S5 in Supporting information). The calibration equations, the coefficients of determination (R^2), linear ranges, relative standard deviations (RSDs), LODs, and LOQs data for 6 organophosphorus pesticides are shown in Table 1. The results indicated that the TAAEAI-MS method had good reproducibility and high precision, and the R^2 numbers were greater than 0.995 and the RSD numbers are less than 9.2%.

Table 1
The calibration equations, R^2, linear ranges, RSDs, LODs, and LOQs of 6 organophosphorus pesticides.

Pesticide	Equation	R^2	Linear range (μg/g)	Concentration (μg/g)	RSD (%)	LOD (μg/g)	LOQ (μg/g)
Chlorpyrifos	$y = 33048x + 680.83$	0.9988	0.1–10	0.1	5.96	0.0142	0.0475
				0.5	3.49		
				2	2.15		
				5	2.84		
				10	2.53		
Dichlorvos	$y = 44654x + 698.68$	0.9969	0.1–10	0.1	2.53	0.0124	0.0413
				0.5	4.43		
				2	3.23		
				5	1.89		
				10	4.91		
Dimethoate	$y = 34098x + 964.70$	0.9974	0.1–10	0.1	6.25	0.0216	0.0721
				0.5	7.87		
				2	4.43		
				5	2.60		
				10	6.58		
Malathion	$y = 73365x + 1617.2$	0.9969	0.1–10	0.1	7.69	0.0245	0.0817
				0.5	3.99		
				2	2.42		
				5	4.97		
				10	3.76		
Profenofos	$y = 47272x + 455.62$	0.9985	0.1–10	0.1	5.20	0.0136	0.0454
				0.5	5.42		
				2	3.17		
				5	7.38		
				10	2.55		
Trichlorfon	$y = 34583x + 399.44$	0.9969	0.1–10	0.1	8.90	0.0169	0.0564
				0.5	6.12		
				2	8.02		
				5	7.04		
				10	9.14		

The mixed standard solution was spiked at the concentration of 0.05 μg/g to strawberry juice sample, and the LODs and LOQs were correspondingly measured. The LODs and LOQs of 6 pesticides range from 0.0124 μg/g to 0.0245 μg/g and from 0.0413 μg/g to 0.0817 μg/g, respectively. Except dimethoate, other pesticides′ LODs were lower than the maximum residue limits (MRLs) of the National Food Safety Standards of the People's Republic of China No. 2763–2021 (GB 2763–2021) and the European Parliament and Council Regulations No. 149/2008 (EC 149/2008) [42,43]. Thus, the method established here could be used to determine whether the contents of pesticide residues in fruits and vegetables exceed the national standards.

Three strawberry samples were obtained from local markets. The juices were squeezed from the strawberries. The TAAEAI-MS method was then used to detect possible pesticides in these juice samples. Each sample was analyzed in triplicate, and the average content and the recovery were determined according to the established calibration curves (Table 1). The results showed that three organophosphorus pesticides were detected in three strawberry samples. Sample 1 contains profenofos residue, sample 2 contains malathion residue, and sample 3 contains both profenofos and malathion residues (Table 2 and Fig. S6 in Supporting information). Sample 3 also contains non-quantifiable chlorpyrifos residue. The contents of profenofos in samples 1 and 3 exceed the MRL of EC 149/2008 by 190% and 128%, respectively, while the contents of malathion in samples 2 and 3 are lower than the MRL. The standard addition experiments were also carried out for three strawberry samples to measure the recovery. The addition concentrations for each pesticide were 0.1 μg/g and 0.5 μg/g, respectively. The recoveries ranged from 82.6% to 116% (Table 2).

To examine whether washing could reduce the amount of pesticide residues in strawberries, we thoroughly washed three strawberry samples with deionized water and performed the analysis again. The results showed that the contents of profenofos in samples 1 and 3 greatly reduced and were not detected by our method. The amount of malathion residues in samples 2 and 3 also reduced to a non-quantifiable level. These results suggested that washing can effectively reduce and even remove pesticide residues from strawberry products. Therefore, although samples 1 and 3 contain profenofos exceeding the MRL, they are still edible after thorough washing.

We compared TAAEAI-MS with other AMS techniques developed in recent years to assess their performances in pesticide detection (Table S1 in Supporting information). These AMS techniques include thermal desorption electrospray ionization-MS (TD-ESI-MS), PSI-MS, wooden-tip electrospray ionization-MS (Wooden-tip ESI-MS), leaf spray ionization-MS (LSI-MS), DART-MS, and electrospray laser desorption ionization-MS (ELDI-MS) [44–49]. PSI-MS has low LODs and LOQs but requires complicated sample pretreatment such as extraction and separation thus is time-consuming and resource-demanding. Some AMS techniques can directly analyze sample without pretreatment or only with simple pretreatment (no extraction and separation). However, due to matrix effect, the performances of these AMS techniques fluctuate greatly, and the LOD sometimes can even reach as high as 1000 μg/L. In contrast, TAAEAI-MS can directly detect pesticides in strawberry juice sample with no need of sample extraction and separation, and the detection performance is not largely compromised by complex matrices in strawberry. TAAEAI-MS are significantly better than other direct injection AMS techniques in LODs and LOQs, and even comparable to PSI-MS. In addition, the analysis time of TAAEAI-MS is extremely short. It takes only a few seconds for the entire process from sampling to data collection, which is very valuable for rapid, real-time application. Therefore, TAAEAI-MS has advantages in pesticide detection, especially suitable for those samples containing complex matrices. In addition, TAAEAI can be applied to efficiently analyze low-polarity pesticides, such as phenoxycycloposphazene and diphenylphosphine oxide in methanol solution (10 μg/g) (Fig. S7 in Supporting information).

Table 2
The contents and recoveries of 6 organophosphorus pesticides in 3 strawberry samples and the MRLs of GB 2763–2021 and EC 149/2008.

Pesticide	Sample 1			Sample 2			Sample 3			MRLs (μg/g)	
	Result (μg/g)	Recovery (%)		Result (μg/g)	Recovery (%)		Result (μg/g)	Recovery (%)		GB 2763–2021	EC 149/2008
Chlorpyrifos	ND[a]	104[d]	89.0[e]	ND	108[d]	85.1[e]	NQ	101[d]	88.0[e]	0.3	0.2
Dichlorvos	ND	105[d]	92.8[e]	ND	93.3[d]	88.8[e]	ND	89.3[d]	110[e]	0.2	0.01
Dimethoate	ND	97.4[d]	89.3[e]	ND	105[d]	110[e]	ND	113[d]	97.1[e]	0.01	0.02
Malathion	ND	91.4[d]	105[e]	0.186	94.3[d]	90.0[e]	0.162	116[d]	96.1[e]	1	/
Profenofos	0.145	103[d]	96.4[e]	NQ[b]	109[d]	88.4[e]	0.114	109[d]	92.7[e]	/[c]	0.05
Trichlorfon	ND	98.3[d]	103[e]	ND	92.5[d]	114[e]	ND	98.6[d]	82.6[e]	0.2	2

[a] ND, not detected.
[b] NQ, not quantified.
[c] /, not mentioned in the literature.
[d] The added standard concentration was 0.1 μg/g.
[e] The added standard concentration was 0.5 μg/g.

In summary, a TAAEAI-MS method was developed in this work, which combines microsyringe tip sampling and electric arc ionization for direct juice sample analysis. This method was successfully applied to rapidly measure organophosphorus pesticides in strawberry with good quantitative performance, good repeatability, high precision, high sensitivity, and low matrix interference. In the future, TAAEAI-MS might have potential to be a routine analysis method for the detection of pesticide residues in fruits and vegetables.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.12.029.

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