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Simultaneous Screening of 733 Pesticide Residues in Fruits and Vegetables by a GC/LC-Q-TOFMS Combination Technique

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ABSTRACT

In this paper, we report the construction of two accurate mass databases and the development of a combination detection method that simultaneously screens for 733 pesticide and chemical contaminant multi-residues via high-throughput liquid chromatography (LC)- and gas chromatography (GC)-quadru pole-time-of-flight mass spectrometry (Q-TOFMS). This work demonstrates that electronic mass spectral standards may replace chemical-source standard materials as references through one sample preparation and the combination of GC/LC-Q-TOFMS screening. This cutting-edge technique has also replaced multi-residue determination using targeted detection with non-targeted screening. The pesticide residue types, sensitivity, recovery, and reproducibility of this combination technique are evaluated in eight fruit and vegetable matrices. This technique shows three advantages: ① In comparison with the discovery capability of a single technique, the combination technique shows an improvement of 51.1% (GC-Q-TOFMS) and 39.6% (LC-Q-TOFMS), respectively; ② the combination technique can satisfy a screening limit lower than $10 \mu\text{g}\cdot\text{kg}^{-1}$ and meet the requirements of “uniform standards,” although some of the pesticide residues could be optimized to further improve screening sensitivity; ③ over 488 pesticides with recoveries between 60%–120% and relative standard deviation (RSD) < 20% at a spiked level of $10 \mu\text{g}\cdot\text{kg}^{-1}$ were detected with the combination technique in eight different matrices. From 2012 to 2017, this combination technique was applied in an investigation to screen pesticide residues from 1384 sampling locations for 38 138 batched samples covering 18 categories and 134 types of fruits and vegetables obtained from across the mainland of China. After statistical analysis, 533 pesticides in 115 891 determinations were detected, and the regularity of pesticides in the fruits and vegetables sold on the Chinese market was shown.

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1. Introduction

In the process of plant growth, pesticides are used on fruits and vegetables to increase product output and prevent plant diseases and pest infestation [1]. The direct or indirect application of pesticide-contaminated products may lead to the accumulation of pesticides in the body; even at low concentrations, it may cause serious illnesses such as disorders of the reproductive and endocrine systems, cancers, kidney diseases, Parkinson's disease, Alzheimer's disease, and more [2–7]. Therefore, the possible effect of pesticide residues on public health has become a global concern

[8]. Due to geographic and dietary habits, fruit and vegetable consumption in different countries and regions varies, and the pesticide types used and residual levels may also differ. As a result, pesticide residue detection faces tremendous challenges: The matrix types of fruits and vegetables are complex and various, the number of pesticides is large, the physical and chemical properties of pesticides differ, and the pesticide content is relatively low. It is urgent to develop a high-throughput, highly sensitive, and general detection method to determine pesticide residues in fruits and vegetables.

Gas chromatography (GC) and liquid chromatography (LC) methods are common approaches for pesticide residue quantitative determination [9–11], and include the GC-nitrogen phosphate detector (NPD), GC-flame photometric detector (FPD) [12,13], LC-ultraviolet detector (UVD), and LC-fluorescent detector

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[14,15]. However, these methods are mainly used for a single type of pesticide residue analysis; furthermore, the number of target analytes is low, and the sensitivity usually cannot meet the trace element detection level (ppb), and thus cannot satisfy the pesticide multi-residues requirements of high-throughput and non-target detection on bulky batched samples. Our group performed a literature search and collected 4109 papers on pesticide residues published in 15 major international journals over the past 24 years (1990–2013). We found that the number of papers based on chromatography—which had once dominated in the field of pesticide residue analysis—had been exceeded by papers based on mass spectrometry (MS), indicating that the MS technique has been rapidly developed for pesticide residue detection [16]. GC and LC coupled with MS detectors such as sector magnetic detectors [17], orbitrap detectors [18], ion trap detectors [19], and time-of-flight (TOF) detectors [20] can be used for the high-throughput analysis of pesticide multi-residues in complex matrices. Quadrupole-time-of-flight mass spectrometry (Q-TOFMS), which has high resolution, a high scan speed, and a full scan spectra, can be used to obtain plenty of ions with accurate mass [21], which can improve the identification and detection levels of compounds [22–24]; therefore, Q-TOFMS is one of the most widely used techniques for the non-target detection of pesticide multi-residues in a complex matrix [25–27]. In 2004, Hernández et al. [28] used Q-TOFMS for the accurate quantification of organic trace multi-elements in earth surface water, thereby demonstrating that Q-TOFMS could potentially be applied to the quantitative analysis of targeted trace elements in environmental samples. Therefore, LC-Q-TOFMS and GC-Q-TOFMS will ensure a promising prospect for application in the non-targeted screening and quantification detection of pesticide multi-residues in complex matrices. There are 96 reports on pesticide residues screening using GC/LC-Q-TOFMS published in 15 journals in 2016; as early as 2007, Grimalt et al. [29] reported on the determination of two pesticide residues in fruits and vegetables using LC-Q-TOFMS. Wang and Leung [30] used LC-Q-TOFMS to screen for pesticides in full-scan mode, and established an analysis method for 138 pesticides in fruit- and vegetable-based infant foods. After the first application of GC-Q-TOFMS in the field of pesticide residue analysis in 2010 [31], Zhang et al. [32] developed a screening and confirmation method for the determination of 187 pesticides in vegetables by means of GC-Q-TOFMS in 2012. The results showed that GC-Q-TOFMS is reliable for pesticide confirmation. Wang et al. and Hernández et al. developed a GC-Q-TOFMS screening method for over 100 pesticide residues and chemical contaminants in fruits and vegetables [23,33], feeds, and fish [34]. The abovementioned results demonstrate that the LC/GC-Q-TOFMS method has a wide screening range, provides accurate quantification of target compounds, possesses good adaptability to matrices as well as high sensitivity, and can be used to improve the number of pesticides detected and the detection capability in comparison with chromatography techniques. LC-Q-TOFMS is applicable to involatile and medium/strong polarity compounds, while GC-Q-TOFMS is applicable to volatile/semi-volatile and non/low-polarity compounds; thus, each technology has its own applicable scope. Developing a combined application of GC/LC-Q-TOFMS is the trend for comprehensive, high throughput, and non-targeted pesticide multi-residue detection.

This research is based on the construction of accurate pesticide mass databases using LC-Q-TOFMS and GC-Q-TOFMS. For the first time, we report the development of a method based on the combination of GC/LC-Q-TOFMS that can simultaneously screen 733 pesticide residues in various types of fruits and vegetables; we also present a comparison of the limit of screening detection and recovery efficiency for various practical samples in order to verify the detection capability of the combination technique. The detection capability of the combination technique (i.e., 733 pesticides) is

significantly greater than those of single techniques; it is 51.1% greater in comparison with GC-Q-TOFMS (485 pesticides), and 39.6% greater in comparison with LC-Q-TOFMS (525 pesticides). With this combination technique, LC-Q-TOFMS and GC-Q-TOFMS not only bring their own unique advantages, but also complement each other by verification through co-detected pesticides and provide an internal quality-control standard to ensure the reliability of test results. An investigation of the pesticide residues in fruit and vegetable samples was carried out from 2012 to 2017 across 31 provincial capitals or municipalities in China using this combination technique. In a total of 38 138 batches of fruit and vegetable samples covering 18 categories and 134 types of fruits and vegetables from 1384 sampling locations on the market, 533 pesticides were detected in 115 891 determinations. This study provides data showing the basic status of pesticide residues in fruits and vegetables in China, and thus offers strong technical support for pesticide management and control.

2. Experiments

2.1. Sample pretreatment

The following procedure was used for sample pretreatment [35,36]: Weigh a 10 g sample (± 0.01 g) into an 80 mL centrifuge tube. Add 40 mL 1% acetate-acetonitrile solution and homogenize at $12\,000\text{ r}\cdot\text{min}^{-1}$ for 1 min; then add 1 g NaCl and 4 g dehydrated MgSO_4 , and shake for 10 min. Centrifuge at $4200\text{ r}\cdot\text{min}^{-1}$ for 5 min, then transfer 20 mL of supernatant into a pear-shaped flask and rotarvap in a $40\text{ }^\circ\text{C}$ water bath until about 2 mL is left and wait for cleanup.

Add Na_2SO_4 to a carbon/ NH_2 cartridge with a height of about 2 cm. Use 4 mL of a mixture of acetonitrile/toluene (3:1, v/v) to rinse the solid-phase extraction (SPE) cartridge, and discard the effluents. Load this concentrated sample solution into the cleanup cartridge, using a pear-shaped flask to collect the elute. Add 2 mL of acetonitrile/toluene (3:1, v/v) to the concentrated flask and transfer the rinsing fluids into the SPE cartridge. Connect a 25 mL reservoir to the cartridge and rinse with 25 mL acetonitrile/toluene (3:1, v/v). Rotarvap the elute to about 0.5 mL in a $40\text{ }^\circ\text{C}$ water bath. Dry the concentrations under nitrogen flow, and then add 2 mL acetonitrile/toluene (3:1, v/v); ultrasound re-dissolve and vortex, and separate into two equal portions of 1 mL each. Re-dry under nitrogen flow. Use 1 mL of 1% formic acid-acetonitrile/water (2:8, v/v) or 1 mL of hexane to re-dissolve, and then filter with a $0.22\text{ }\mu\text{m}$ nylon membrane to prepare for LC-Q-TOFMS or GC-Q-TOFMS.

2.2. Construction of database and establishment of digital detection techniques

2.2.1. Construction of the LC-Q-TOFMS database

Inject $10\text{ }\mu\text{L}$ of $1\text{ mg}\cdot\text{L}^{-1}$ single standard solution into the LC-Q-TOFMS in MS mode. Process the experimental data using Agilent qualitative software and the “Find by Formula” function. The compound is considered to be identified when the target compound score is over 90 and the accurate mass error is lower than 5 ppm. Record the retention time and ionization forms ($[\text{M} + \text{H}]^+$, $[\text{M} + \text{NH}_4]^+$, and $[\text{M} + \text{Na}]^+$) (M refers to a molecular ion) of the peak under chromatographic separation conditions. Archive the name, chemical equation, accurate molecular weight, and retention time of each pesticide into the database as one observation. The accurate mass database of LC-Q-TOFMS includes 525 pesticides. The spectra library was developed using the Agilent MassHunter personal compound database and library (PCDL) manager (B.07.00), as follows: Collect data in the “Targeted MS/MS” mode by inputting each pesticide’s retention time, parent ion, and fragment ions

at eight different collision energies. Use the “Find by Targeted MS/MS” function to process the data, and acquire the fragment ions full-scan spectra at different collision energy levels. Generate a .CEF format file. Introduce the .CEF format files into the PCDL manager software; select four spectra under the optimum collision energies and save them with the corresponding pesticide information. In this way, the spectra library of LC-Q-TOFMS for 525 pesticides was constructed. (Information on these 525 pesticides is provided in [Supplementary Table S1.](#))

2.2.2. Construction of the GC-Q-TOFMS database

An accurate mass database for GC-Q-TOFMS was developed using the Agilent MassHunter PCDL manager (B.07.00): Inject 1 μL of 1 $\text{mg}\cdot\text{L}^{-1}$ single standard solution into the GC-Q-TOFMS under the MS mode. Acquire the primary mode full-scan data in the qualitative software and record the retention time of the compound peak under the chromatographic separation condition. In the “Search Library” function, identify the compound by means of the National Institute of Standards and Technology (NIST) database in order to extract information such as the name, molecular formula, accurate molecular mass, fragment ions, and so forth. After the information on the accurate mass of the ion in the spectra is verified and confirmed, introduce the edited spectra and compound information to PCDL manager and link them with the corresponding pesticide information in order to construct the primary fragment ions spectra database. In this way, the primary fragment ions spectra database was constructed for 485 pesticides and chemical contaminants. (Information on these 485 pesticides is provided in [Supplementary Table S2.](#))

2.2.3. Development of the digital detection technique

A unique electronic identity card was established for each of the 733 pesticides that are commonly used around the world. This is the theoretical basis for the creation of an electronic standard that can take the place of conventional standard material as a reference. Each electronic identity card consists of the following information: retention time, primary adduct ion accurate mass, isotope distribution, isotope abundance, secondary fragmented accurate mass, and spectra.

An automatic matching qualitative identification software for pesticide residue MS was developed. The acquisition data result is compared with the pesticide database. The software realizes high speed (ca. 0.5 h) (identification and confirmation for per sample), high throughput (525/485 pesticides), high precision (0.0001 m/z), high reliability, high informatization, and high automation, which can improve the method efficiency.

2.3. Screening strategy

Based on the database and our group's data-retrieval conditions, as reported previously, MassHunter software was adopted for the screening of pesticide residues in fruits and vegetables.

For the LC-Q-TOFMS [35], primary accurate mass database retrieval was first adopted, with the parameters set as follows: a retention time window of ± 0.5 min; accurate mass errors of ± 10 ppm; and the ionization forms $[M + H]^+$, $[M + \text{NH}_4]^+$, and $[M + \text{Na}]^+$ for data retrieval. Based on the results from the accurate mass, retention time, isotope distribution, and abundance, the software computes the errors of the practical values with the theoretical values and provides a score matching the retrieval result. For a result scoring ≥ 70 , the compound was temporarily determined to be the suspected pesticide. Then the parent ion, retention time, and optimum collision energy of the suspected ion were input for instrumental determination, and the suspected pesticide was confirmed and processed by the spectra library under the “Targeted MS/MS” mode. The retrieval parameters were set to the reverse

phase-matching mode and to matching results through mirror-image symmetry. If the value was greater than 70, positive detection was instantly confirmed.

For the GC-Q-TOFMS [36], through primary spectra library retrieval was applied, and characteristic ions were extracted by the Agilent qualitative software and the “Find Compound by Formula” function for a specific retention time. After extraction, all the eligible compounds under the retrieval conditions and their characteristic ions were displayed. During this process, the retrieval conditions were set as follows: a retention time window of ± 0.25 min, a mass error of ± 10 ppm, and two characteristic ions detected, the ion abundance ratio error was below 30%.

2.4. Quantification

A single point external standard was adopted for pesticide quantification. Based on the maximum residue limits (MRLs) of pesticides in fruits and vegetables, a concentration matrix matching standard of 1.5 times the MRL was prepared, and the single point calibration method was employed for target pesticide quantification. If the pesticide concentration determined was greater than 2.25 times the MRL, a closer concentration matrix matching standard was re-prepared based on the analytical results for re-quantification of the target compound. When the pesticide concentrations detected in the samples were extremely high, causing saturation of the detectors, the sample matrix and matrix matching standard were equally diluted to obtain accurate quantification.

2.5. Method efficiency evaluation protocol

To evaluate the efficiency and verify the sensitivity, linearity, and wide applicability of the non-targeted and high-throughput pesticide screening method combining GC-Q-TOFMS and LC-Q-TOFMS, eight types of fruits and vegetables were chosen.

2.5.1. Matrix selection

Due to the varieties of fruits and vegetables on the market, the matrix selected was representative. The following eight matrices were chosen: apple, grape, watermelon, grapefruit, spinach, tomato, head cabbage, and celery. These fruits and vegetables were chosen to cover kernel, citrus, berry, and melon fruits; and leafy, solanum, and brassica vegetables.

2.5.2. Detailed implementation protocol

For the LC-Q-TOFMS, matrix spiked experiments were conducted at five concentration levels—1, 5, 10, 20, and 50 $\mu\text{g}\cdot\text{kg}^{-1}$ —to investigate the screening detection limits (SDLs) of the 525 pesticides. In the meantime, spiked recovery experiments were carried out at three concentration levels—5, 10, and 20 $\mu\text{g}\cdot\text{kg}^{-1}$ —to investigate the recoveries and precision of the 525 pesticides.

For the GC-Q-TOFMS, matrix spiked experiments were conducted at six concentration levels—1, 5, 10, 20, 50, and 100 $\mu\text{g}\cdot\text{kg}^{-1}$ —to investigate the SDLs of the 485 pesticides. In the meantime, spiked recovery experiments were conducted at three concentration levels—10, 50, and 100 $\mu\text{g}\cdot\text{kg}^{-1}$ —to investigate the recoveries and precision of the 485 pesticides.

2.6. Application demonstrations

All the fruit and vegetable samples ($n = 38\ 138$) were obtained from super- or agro-product markets across 31 Chinese provinces/municipalities, with over 1384 sampling locations (details in [Table 1](#)). The samples covered 18 categories and 134 types of fruits and vegetables (see [Table 2](#)). Only the edible parts of the fruits and vegetables were sampled; the samples were cut into pieces and homogenized for sample pretreatment.

Table 1

Geographical range of pesticide detection: 31 provinces/municipalities in China, with 38 138 samples and 1384 sampling locations.

| No. | Provinces/municipalities | Number of samples | Number of locations | No. | Provinces/municipalities | Number of samples | Number of locations |
|-----|--------------------------|-------------------|---------------------|-------|--------------------------|-------------------|---------------------|
| 1 | Beijing | 5464 | 177 | 17 | Jilin | 869 | 19 |
| 2 | Shandong | 3144 | 156 | 18 | Shaanxi | 845 | 39 |
| 3 | Tianjin | 2820 | 72 | 19 | Chongqing | 833 | 34 |
| 4 | Hebei | 2802 | 54 | 20 | Anhui | 750 | 40 |
| 5 | Guangdong | 2152 | 109 | 21 | Gansu | 676 | 21 |
| 6 | Shanghai | 1707 | 66 | 22 | Hunan | 676 | 35 |
| 7 | Hainan | 1440 | 40 | 23 | Shanxi | 657 | 26 |
| 8 | Jiangsu | 1279 | 43 | 24 | Guangxi | 643 | 14 |
| 9 | Zhejiang | 1259 | 34 | 25 | Jiangxi | 629 | 35 |
| 10 | Sichuan | 1232 | 43 | 26 | Guizhou | 556 | 30 |
| 11 | Yunnan | 1109 | 30 | 27 | Inner Mongolia | 483 | 28 |
| 12 | Henan | 1055 | 51 | 28 | Xinjiang Uygur | 423 | 23 |
| 13 | Liaoning | 935 | 26 | 29 | Qinghai | 350 | 13 |
| 14 | Fujian | 927 | 19 | 30 | Ningxia | 331 | 16 |
| 15 | Heilongjiang | 922 | 35 | 31 | Tibet | 265 | 9 |
| 16 | Hubei | 905 | 47 | Total | | 38 138 | 1384 |

Table 2

The analyzed 134 types and the sample numbers.

| No. | Sample | Number | No. | Sample | Number | No. | Sample | Number |
|-------------------|------------------------|--------|-----|-----------------------------------|--------|--------------|------------------------------|--------|
| Vegetables | | | 46 | Pumpkins | 172 | Fruit | | |
| 1 | Eggplant | 1303 | 47 | Water spinach | 160 | 91 | Dragon fruit | 804 |
| 2 | Sweet pepper | 1241 | 48 | Choisum (flowering white cabbage) | 149 | 92 | Kiwifruit | 754 |
| 3 | Carrot | 739 | 49 | Celtuce | 135 | 93 | Watermelon | 540 |
| 4 | Spinach | 727 | 50 | Endive | 99 | 94 | Lemon | 487 |
| 5 | Bulb onion | 466 | 51 | Amaranth | 85 | 95 | Plum | 345 |
| 6 | Garland chrysanthemum | 422 | 52 | Chinese broccoli | 77 | 96 | Strawberry | 337 |
| 7 | Cauliflower | 321 | 53 | Ginger | 75 | 97 | Pineapple | 238 |
| 8 | Smooth loofah | 302 | 54 | Lotus rhizome | 75 | 98 | Muskmelon | 185 |
| 9 | Garlic scape | 246 | 55 | Yam | 74 | 99 | Papaya | 149 |
| 10 | Green onion | 161 | 56 | Garlic | 66 | 100 | Tangerine | 57 |
| 11 | Fennel leaf | 154 | 57 | Purple potato | 66 | 101 | Apricot | 40 |
| 12 | Cowpea | 110 | 58 | Taro | 62 | 102 | Nectarine | 26 |
| 13 | Baby Chinese cabbage | 86 | 59 | Sweet potato | 60 | 103 | Passion fruit | 7 |
| 14 | Mustard greens | 60 | 60 | Chayote | 54 | 104 | Apple | 1629 |
| 15 | Soya bean (young pods) | 33 | 61 | Pepino | 51 | 105 | Pear | 1513 |
| 16 | Bamboo shoots | 33 | 62 | Sweet potato leaves | 48 | 106 | Grape | 1164 |
| 17 | Hyacinth bean | 31 | 63 | Green garlic | 46 | 107 | Sweet orange | 818 |
| 18 | Watercress | 29 | 64 | Spring vegetable | 40 | 108 | Peach | 726 |
| 19 | Yellow garlic sprout | 25 | 65 | Milk cabbage | 33 | 109 | Mandarin orange | 514 |
| 20 | Mung bean sprouts | 19 | 66 | Bottle gourd | 29 | 110 | Mango | 512 |
| 21 | Okra | 14 | 67 | Asparagus | 27 | 111 | Banana | 357 |
| 22 | Rooted mustard sprout | 8 | 68 | Indian spinach | 27 | 112 | Hami melon | 229 |
| 23 | Boxthorn leaves | 7 | 69 | Chinese toon sprouts | 26 | 113 | Pummelo | 172 |
| 24 | Gynura bicolor | 7 | 70 | Podded pea | 24 | 114 | Chinese Jujube | 171 |
| 25 | Winter squash | 5 | 71 | Lily | 17 | 115 | Litchi | 140 |
| 26 | Radish sprout | 1 | 72 | Garden pea | 17 | 116 | Melon (honeydew) | 116 |
| 27 | Tomato | 1590 | 73 | Water bamboo | 15 | 117 | Longan | 68 |
| 28 | Cucumber | 1586 | 74 | Taro flower | 10 | 118 | Carambola | 62 |
| 29 | Celery | 1262 | 75 | Toothed burclover | 5 | 119 | Chinese persimmon | 61 |
| 30 | Common bean | 1228 | 76 | Yacon | 5 | 120 | Guava | 40 |
| 31 | Head lettuce | 1124 | 77 | Soybean sprouts | 4 | 121 | Loquat | 34 |
| 32 | Head cabbage | 970 | 78 | Chinese chive's flower | 3 | 122 | Kumquats | 28 |
| 33 | Zucchini | 943 | 79 | Water chestnut | 2 | 123 | Mayhaw | 28 |
| 34 | Chinese chive | 926 | 80 | Sword bean | 2 | 124 | Pomegranate | 26 |
| 35 | Napa cabbage | 695 | 81 | Chinese celery | 2 | 125 | Wax jambu | 9 |
| 36 | Wax gourd | 671 | 82 | Chinese flat cabbage | 2 | 126 | Blueberry | 2 |
| 37 | Leaf lettuce | 625 | 83 | Chinese radish | 447 | 127 | Durian | 1 |
| 38 | Bok choy | 498 | 84 | Broccoli | 762 | 128 | Mulberry | 1 |
| 39 | Rape greens | 461 | 85 | Shiitake mushroom | 238 | 129 | Red bayberry | 1 |
| 40 | Chili pepper | 386 | 86 | <i>Pleurotus eryngii</i> | 224 | 130 | Mangosteen | 127 |
| 41 | Balsam pear | 367 | 87 | Oyster mushroom | 68 | 131 | Sweet cherry | 51 |
| 42 | Potato | 325 | 88 | Mushroom | 480 | Other | | |
| 43 | Red cabbage | 319 | 89 | Enoki mushroom | 299 | 132 | Coriander leaf | 106 |
| 44 | Green Chinese cabbage | 306 | 90 | Wood ear | 2 | 133 | Mint | 2 |
| 45 | Cherry tomato | 226 | | | | 134 | Sweet corn (corn on the cob) | 39 |

3. Results and discussion

3.1. Linearity

Standard curves were studied in the range of 1–500 $\mu\text{g}\cdot\text{L}^{-1}$ at nine concentration levels: 1, 2, 5, 10, 20, 50, 100, 200, and 500 $\mu\text{g}\cdot\text{L}^{-1}$ (Figs. 1 and 2). The linear correlation coefficient was good ($R^2 \geq 0.995$) for 96.1% of the pesticides by LC-Q-TOFMS and for 92.4% of the pesticides by GC-Q-TOFMS.

For LC-Q-TOFMS, Fig. 1 shows a good linear correlation coefficient for 305 pesticides (58.1%) in the linearity range of 1–500 $\mu\text{g}\cdot\text{L}^{-1}$, and for a total of 189 pesticides (36.0%) in the linearity ranges of 2–500, 5–500, 10–500, 20–500, 50–500, 1–200, 1–100, 2–200, 5–200, 10–200, and 20–200 $\mu\text{g}\cdot\text{L}^{-1}$, except for 20 pesticides with low sensitivity. For GC-Q-TOFMS, Fig. 2 displays a good linear correlation coefficient for a total of 448 pesticides (92.4%) at a corresponding analytical concentration range, except for 37 pesticides with low sensitivity, which have a linearity range outside of 1–500 $\mu\text{g}\cdot\text{L}^{-1}$.

3.2. Screening detection limits

Single and combination techniques were studied to determine the SDLs of 733 pesticides in eight matrices at six concentration levels: 1, 5, 10, 20, 50, and 100 $\mu\text{g}\cdot\text{kg}^{-1}$. (Details are listed in Supplementary Tables S1 and S2, as well as in Table 3 and Fig. 3.)

Table 3 and Fig. 3 show 256–313 pesticide SDLs at 1 $\mu\text{g}\cdot\text{kg}^{-1}$ for LC-Q-TOFMS and only 71–133 pesticide SDLs for GC-Q-TOFMS in the eight matrices; this result testifies to the advantage of a concentration of 1 $\mu\text{g}\cdot\text{kg}^{-1}$ for LC-Q-TOFMS. There are 194–253 pesticides at 5 $\mu\text{g}\cdot\text{kg}^{-1}$ for GC-Q-TOFMS, but only 66–128 pesticides for LC-Q-TOFMS, demonstrating the advantage of a concentration of 5 $\mu\text{g}\cdot\text{kg}^{-1}$ for GC-Q-TOFMS. As shown in Table 3, the 10 $\mu\text{g}\cdot\text{kg}^{-1}$ “uniform standard” was adopted to evaluate the SDL of the screening method. There are 399 pesticides (82.3%) in grape, which is the largest number of pesticides with SDLs $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$, and 348 pesticides (71.8%) in celery, which is the smallest number of pesticides with SDLs $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$ among the eight selected matrices by GC-Q-TOFMS. Among the eight selected matrices by LC-Q-TOFMS, there are 430 pesticides (81.9%) in celery, which is the largest number of pesticides with SDLs $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$, and 384 pesticides (73.1%) in grape, which is the smallest number of pesticides with SDLs $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$. Therefore, it can be concluded that the GC-Q-TOFMS and LC-Q-TOFMS together can ensure more than 70%

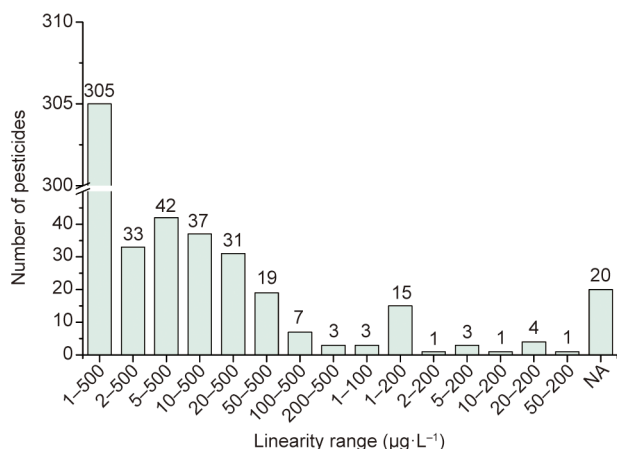


Fig. 1. Distribution of 525 pesticides in different linearity ranges of concentration for LC-Q-TOFMS. NA: not available.

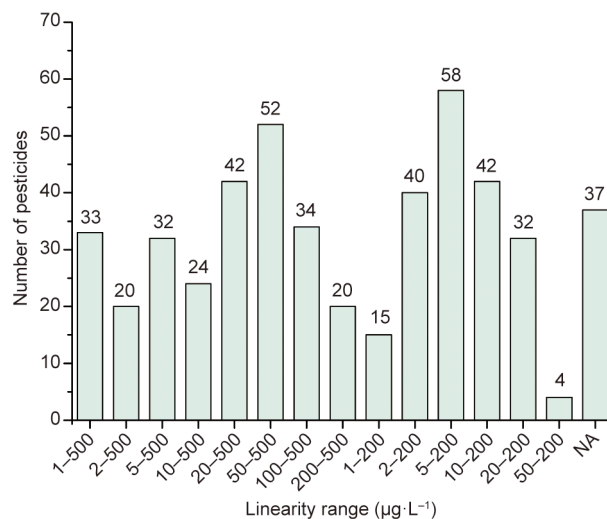


Fig. 2. Distribution of 485 pesticides in different linearity ranges of concentration for GC-Q-TOFMS.

pesticide SDL at a concentration of 10 $\mu\text{g}\cdot\text{kg}^{-1}$ and can thus meet the requirements of the most stringent international MRL standard. With the combination technique, 574 (apple) to 612 (watermelon) pesticide SDLs $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$ were detected, accounting for 78.3%–83.5%. This finding shows that over 78% of pesticides can be detected at $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$, which increases not only the number of pesticide varieties that can be detected but also the method's sensitivity by 8%, thereby demonstrating the high sensitivity, high efficiency, and complementarity of the screening method (Fig. 4).

3.3. Recoveries and relative standard deviation

Table 4 lists pesticide recoveries (Rec.) in the eight selected matrices at three spiked levels for the GC-Q-TOFMS or LC-Q-TOFMS. For GC-Q-TOFMS spiked levels at 10 $\mu\text{g}\cdot\text{kg}^{-1}$, there were 280 (57.7%, celery) to 352 (72.6%, tomato) pesticides, satisfying “Rec. = 60%–120% & relative standard deviation (RSD) $\leq 20\%$ ” in the eight matrices. For LC-Q-TOFMS spiked levels at 5 $\mu\text{g}\cdot\text{kg}^{-1}$, there were 292 (55.6%, grape) to 377 (71.8%, celery) pesticides. For the GC-Q-TOFMS spiked level at 50 $\mu\text{g}\cdot\text{kg}^{-1}$, there were 317 (60.4%, watermelon) to 403 (77.1%, tomato) pesticides, satisfying “Rec. = 60%–120% & RSD $\leq 20\%$ ” in the eight matrices. For the GC-Q-TOFMS spiked level at 100 $\mu\text{g}\cdot\text{kg}^{-1}$, there were 337 (69.5%, grapefruit) to 416 (85.8%, tomato) pesticides, satisfying “Rec. = 60%–120% & RSD $\leq 20\%$,” while for LC-Q-TOFMS spiked level at 20 $\mu\text{g}\cdot\text{kg}^{-1}$, there were 366 (69.7%, grapefruit) to 420 (80.0%, celery) pesticides. Based on the percentages (55.6%–85.8%) of pesticides that comply with “Rec. = 60%–120% & RSD $\leq 20\%$ ” by GC-Q-TOFMS or LC-Q-TOFMS in eight matrices, demonstrating that the method accuracy is relatively high. With the combination technique (733 pesticides), there were 488 (66.6%, grapefruit) to 566 (77.2%, tomato) pesticides conforming to “Rec. = 60%–120% & RSD $\leq 20\%$ ”; these results are better than the single-technique results, demonstrating the complementarity of the combination technique.

3.4. Actual sample analysis

An investigation of the combination technique was conducted on 38 138 batched samples covering 18 categories and 134 types of fruits and vegetables from 1384 sampling locations across 31 provinces/municipalities and 14 main fruit and vegetable

Table 3
Comparison of the screening capability of the two methods for 733 pesticides in eight matrices.

| Methods | Number and proportion of pesticides detected at different concentration level ($\mu\text{g}\cdot\text{kg}^{-1}$) | | | | | | | | Screened pesticides | Unscreened pesticides | Total |
|------------|--|-------------|-------------|------------|------------|------------|-----------|-------------|---------------------|-----------------------|-------|
| | 1 | 5 | 10 | 20 | 50 | 100 | ≤ 10 | | | | |
| Apple | GC-Q-TOFMS + LC-Q-TOFMS | 346 (47.2%) | 165 (22.5%) | 63 (8.6%) | 69 (9.4%) | 36 (4.9%) | 1 (0.1%) | 574 (78.3%) | 680 (92.8%) | 53 (7.2%) | 733 |
| | GC-Q-TOFMS | 133 (27.4%) | 200 (41.2%) | 16 (3.3%) | 64 (13.2%) | 21 (4.3%) | 7 (1.4%) | 349 (72%) | 441 (90.9%) | 44 (9.1%) | 485 |
| | LC-Q-TOFMS | 258 (49.1%) | 80 (15.2%) | 65 (12.4%) | 35 (6.7%) | 56 (10.7%) | | 403 (76.8%) | 494 (94.1%) | 31 (5.9%) | 525 |
| Grape | GC-Q-TOFMS + LC-Q-TOFMS | 366 (49.9%) | 205 (28%) | 31 (4.2%) | 45 (6.1%) | 33 (4.5%) | 5 (0.7%) | 602 (82.1%) | 685 (93.5%) | 48 (6.5%) | 733 |
| | GC-Q-TOFMS | 121 (24.9%) | 245 (50.5%) | 33 (6.8%) | 24 (4.9%) | 14 (2.9%) | 7 (1.4%) | 399 (82.3%) | 444 (91.6%) | 41 (8.4%) | 485 |
| | LC-Q-TOFMS | 287 (54.7%) | 78 (14.9%) | 19 (3.6%) | 52 (9.9%) | 59 (11.2%) | | 384 (73.1%) | 495 (94.3%) | 30 (5.7%) | 525 |
| Watermelon | GC-Q-TOFMS + LC-Q-TOFMS | 363 (49.5%) | 184 (25.1%) | 65 (8.9%) | 31 (4.2%) | 30 (4.1%) | 5 (0.7%) | 612 (83.5%) | 678 (92.5%) | 55 (7.5%) | 733 |
| | GC-Q-TOFMS | 133 (27.4%) | 219 (45.2%) | 40 (8.2%) | 33 (6.8%) | 12 (2.5%) | 5 (1.0%) | 392 (80.8%) | 442 (91.1%) | 43 (8.9%) | 485 |
| | LC-Q-TOFMS | 277 (52.8%) | 66 (12.6%) | 60 (11.4%) | 28 (5.3%) | 56 (10.7%) | | 403 (76.8%) | 487 (92.8%) | 38 (7.2%) | 525 |
| Grapefruit | GC-Q-TOFMS + LC-Q-TOFMS | 311 (42.4%) | 208 (28.4%) | 64 (8.7%) | 52 (7.1%) | 55 (7.5%) | 7 (1.0%) | 583 (79.5%) | 697 (95.1%) | 36 (4.9%) | 733 |
| | GC-Q-TOFMS | 71 (14.6%) | 253 (52.2%) | 34 (7.0%) | 48 (9.9%) | 14 (2.9%) | 13 (2.7%) | 358 (73.8%) | 433 (89.3%) | 52 (10.7%) | 485 |
| | LC-Q-TOFMS | 266 (50.7%) | 83 (15.8%) | 45 (8.6%) | 35 (6.7%) | 82 (15.6%) | | 394 (75%) | 511 (97.3%) | 14 (2.7%) | 525 |
| Spinach | GC-Q-TOFMS + LC-Q-TOFMS | 344 (46.9%) | 203 (27.7%) | 57 (7.8%) | 41 (5.6%) | 38 (5.2%) | 7 (1.0%) | 604 (82.4%) | 690 (94.1%) | 43 (5.9%) | 733 |
| | GC-Q-TOFMS | 128 (26.4%) | 195 (40.2%) | 49 (10.1%) | 33 (6.8%) | 22 (4.5%) | 15 (3.1%) | 372 (76.7%) | 442 (91.1%) | 43 (8.9%) | 485 |
| | LC-Q-TOFMS | 256 (48.8%) | 105 (20.0%) | 39 (7.4%) | 42 (8.0%) | 63 (12.0%) | | 400 (76.2%) | 505 (96.2%) | 20 (3.8%) | 525 |
| Tomato | GC-Q-TOFMS + LC-Q-TOFMS | 382 (52.1%) | 166 (22.6%) | 60 (8.2%) | 40 (5.5%) | 38 (5.2%) | 7 (1.0%) | 608 (82.9%) | 693 (94.5%) | 40 (5.5%) | 733 |
| | GC-Q-TOFMS | 108 (22.3%) | 204 (42.1%) | 60 (12.4%) | 38 (7.8%) | 20 (4.1%) | 10 (2.1%) | 372 (76.7%) | 440 (90.7%) | 45 (9.3%) | 485 |
| | LC-Q-TOFMS | 313 (59.6%) | 76 (14.5%) | 33 (6.3%) | 31 (5.9%) | 55 (10.5%) | | 422 (80.4%) | 508 (96.8%) | 17 (3.2%) | 525 |
| Cabbage | GC-Q-TOFMS + LC-Q-TOFMS | 341 (46.5%) | 183 (25.0%) | 55 (7.5%) | 46 (6.3%) | 47 (6.4%) | 8 (1.1%) | 579 (79.0%) | 680 (92.8%) | 53 (7.2%) | 733 |
| | GC-Q-TOFMS | 111 (22.9%) | 194 (40.0%) | 56 (11.5%) | 39 (8.0%) | 21 (4.3%) | 12 (2.5%) | 361 (74.4%) | 433 (89.3%) | 52 (10.7%) | 485 |
| | LC-Q-TOFMS | 270 (51.4%) | 92 (17.5%) | 34 (6.5%) | 35 (6.7%) | 60 (11.4%) | | 396 (75.4%) | 491 (93.5%) | 34 (6.5%) | 525 |
| Celery | GC-Q-TOFMS + LC-Q-TOFMS | 343 (46.8%) | 215 (29.3%) | 42 (5.7%) | 43 (5.9%) | 36 (4.9%) | 8 (1.1%) | 600 (81.9%) | 687 (93.7%) | 46 (6.3%) | 733 |
| | GC-Q-TOFMS | 93 (19.2%) | 200 (41.2%) | 55 (11.3%) | 37 (7.6%) | 31 (6.4%) | 19 (3.9%) | 348 (71.8%) | 435 (89.7%) | 50 (10.3%) | 485 |
| | LC-Q-TOFMS | 281 (53.5%) | 128 (24.4%) | 21 (4.0%) | 29 (5.5%) | 44 (8.4%) | | 430 (81.9%) | 503 (95.8%) | 22 (4.2%) | 525 |

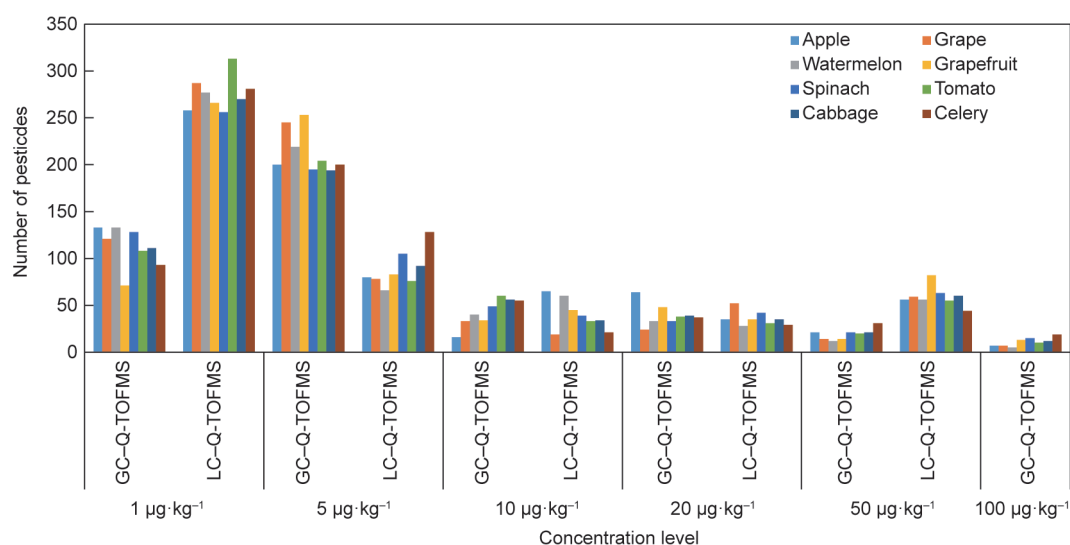


Fig. 3. Number of pesticides detected (SDL) at different spiked levels in eight matrices by GC-Q-TOFMS or LC-Q-TOFMS.

production areas from 2012 to 2017. Using GC-Q-TOFMS, 378 pesticides were detected, and using LC-Q-TOFMS, 315 pesticides were detected, for a total of 553 pesticides, including 160 co-detected pesticides. The 553 detected pesticides are listed in Table 5 according to their functions, chemical compositions, and toxicity.

It can be seen from Table 5, ① insecticides, herbicides, and fungicides are the major pesticides currently used in China, making up 94.7%; ② according to chemical position, the pesticides currently in China are mainly organonitrogen, organophosphorus, organochlorine, carbamate, and pyrethroids, making up

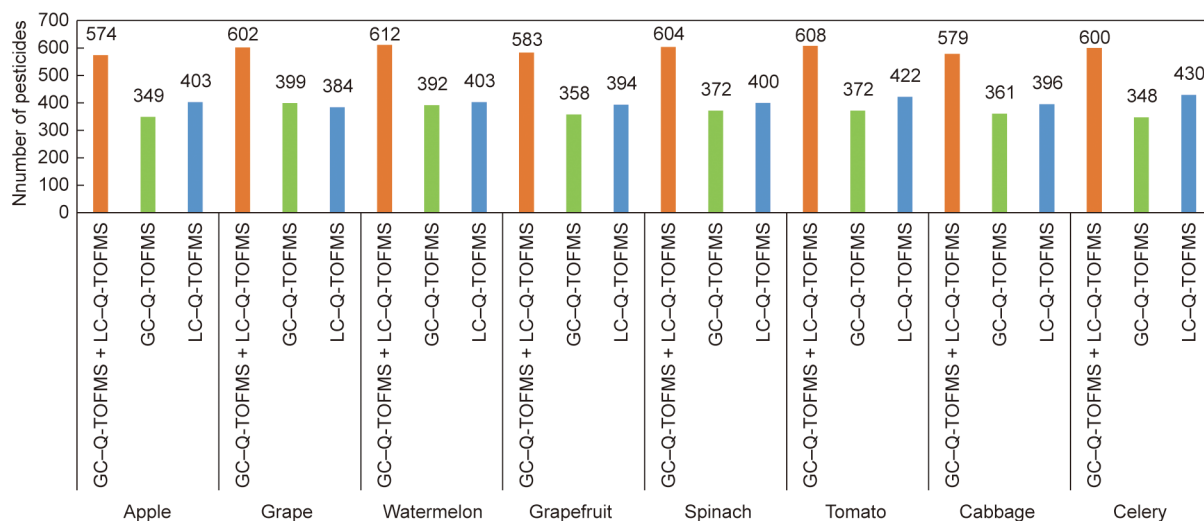


Fig. 4. Number of pesticides detected (SDL) at a spiked concentration level of $\leq 10 \mu\text{g}\cdot\text{kg}^{-1}$ by GC-Q-TOFMS + LC-Q-TOFMS, GC-Q-TOFMS, or LC-Q-TOFMS.

Table 4

Recovery of pesticides at three spiked levels in eight matrices by GC-Q-TOFMS or LC-Q-TOFMS.

| | GC-Q-TOFMS | | | | | | | | LC-Q-TOFMS | | | | | | | | Combined methods Rec. = 60%–120% & RSD $\leq 20\%$, 10 $\mu\text{g}\cdot\text{kg}^{-1}$ | | | |
|------------|---|-----------------|--------|-------------------------|--------|-----------------------------------|--------|---------------|--------------|---|-----------------|--------|-------------------------|--------|-----------------------------------|--------|--|-----|---------------|--------------|
| | Spiked concentration level ($\mu\text{g}\cdot\text{kg}^{-1}$) | Rec. = 60%–120% | | RSD $\leq 20\%$ (n = 3) | | Rec. = 60%–120% & RSD $\leq 20\%$ | | | | Spiked concentration level ($\mu\text{g}\cdot\text{kg}^{-1}$) | Rec. = 60%–120% | | RSD $\leq 20\%$ (n = 3) | | Rec. = 60%–120% & RSD $\leq 20\%$ | | | | | |
| | | NP | PP (%) | NP | PP (%) | NP | PP (%) | Ave. Rec. (%) | Ave. RSD (%) | | NP | PP (%) | NP | PP (%) | NP | PP (%) | | | Ave. Rec. (%) | Ave. RSD (%) |
| Apple | 10 | 313 | 64.5 | 303 | 62.5 | 287 | 59.2 | 89.6 | 10.1 | 5 | 320 | 61.0 | 327 | 62.3 | 313 | 59.6 | 84.8 | 5.5 | 502 | 68.5 |
| | 50 | 396 | 81.6 | 399 | 82.3 | 379 | 78.1 | 93.6 | 6.3 | 10 | 367 | 69.9 | 378 | 72.0 | 363 | 69.1 | 86.1 | 4.7 | | |
| | 100 | 399 | 82.3 | 416 | 85.8 | 388 | 80.0 | 92.3 | 3.7 | 20 | 384 | 73.1 | 394 | 75.0 | 382 | 72.8 | 90.7 | 4.8 | | |
| Grape | 10 | 359 | 74.0 | 356 | 73.4 | 325 | 67.0 | 100.0 | 8.1 | 5 | 308 | 58.7 | 316 | 60.2 | 292 | 55.6 | 83.0 | 5.3 | 536 | 73.1 |
| | 50 | 408 | 84.1 | 394 | 81.2 | 379 | 78.1 | 97.0 | 7.9 | 10 | 349 | 66.5 | 352 | 67.0 | 341 | 65.0 | 87.3 | 5.3 | | |
| | 100 | 415 | 85.6 | 417 | 86.0 | 399 | 82.3 | 100.7 | 6.7 | 20 | 386 | 73.5 | 386 | 73.5 | 373 | 71.0 | 85.6 | 6.2 | | |
| Watermelon | 10 | 361 | 74.4 | 357 | 73.6 | 339 | 69.9 | 93.2 | 5.0 | 5 | 313 | 59.6 | 330 | 62.9 | 312 | 59.4 | 90.0 | 4.4 | 548 | 74.8 |
| | 50 | 400 | 82.5 | 333 | 68.7 | 317 | 65.4 | 91.1 | 8.9 | 10 | 368 | 70.1 | 377 | 71.8 | 364 | 69.3 | 88.5 | 4.6 | | |
| | 100 | 406 | 83.7 | 401 | 82.7 | 386 | 79.6 | 92.0 | 6.0 | 20 | 382 | 72.8 | 395 | 75.2 | 375 | 71.4 | 91.9 | 6.2 | | |
| Grapefruit | 10 | 300 | 61.9 | 343 | 70.7 | 293 | 60.4 | 89.6 | 7.0 | 5 | 299 | 57.0 | 315 | 60.0 | 294 | 56.0 | 90.0 | 5.9 | 488 | 66.6 |
| | 50 | 342 | 70.5 | 390 | 80.4 | 327 | 67.4 | 92.6 | 8.6 | 10 | 325 | 61.9 | 349 | 66.5 | 317 | 60.4 | 93.6 | 6.0 | | |
| | 100 | 353 | 72.8 | 399 | 82.3 | 337 | 69.5 | 93.1 | 6.7 | 20 | 372 | 70.9 | 378 | 72.0 | 366 | 69.7 | 85.2 | 5.3 | | |
| Spinach | 10 | 328 | 67.6 | 343 | 70.7 | 313 | 64.5 | 94.6 | 8.1 | 5 | 313 | 59.6 | 333 | 63.4 | 309 | 58.9 | 82.9 | 5.6 | 525 | 71.6 |
| | 50 | 383 | 79.0 | 356 | 73.4 | 340 | 70.1 | 87.6 | 8.6 | 10 | 360 | 68.6 | 349 | 66.5 | 336 | 64.0 | 88.8 | 7.0 | | |
| | 100 | 400 | 82.5 | 388 | 80.0 | 366 | 75.5 | 91.5 | 6.6 | 20 | 405 | 77.1 | 411 | 78.3 | 395 | 75.2 | 92.0 | 7.7 | | |
| Tomato | 10 | 360 | 74.2 | 357 | 73.6 | 352 | 72.6 | 89.5 | 7.4 | 5 | 343 | 65.3 | 365 | 69.5 | 336 | 64.0 | 90.3 | 6.0 | 566 | 77.2 |
| | 50 | 415 | 85.6 | 408 | 84.1 | 403 | 83.1 | 92.0 | 6.8 | 10 | 387 | 73.7 | 394 | 75.0 | 382 | 72.8 | 91.2 | 6.1 | | |
| | 100 | 421 | 86.8 | 426 | 87.8 | 416 | 85.8 | 90.8 | 6.2 | 20 | 417 | 79.4 | 428 | 81.5 | 415 | 79.0 | 90.8 | 5.8 | | |
| Cabbage | 10 | 342 | 70.5 | 330 | 68.0 | 317 | 65.4 | 90.3 | 6.4 | 5 | 332 | 63.2 | 356 | 67.8 | 331 | 63.0 | 89.9 | 4.4 | 521 | 71.1 |
| | 50 | 391 | 80.6 | 375 | 77.3 | 361 | 74.4 | 91.0 | 5.5 | 10 | 340 | 64.8 | 387 | 73.7 | 339 | 64.6 | 89.3 | 4.6 | | |
| | 100 | 400 | 82.5 | 397 | 81.9 | 379 | 78.1 | 88.6 | 7.4 | 20 | 388 | 73.9 | 413 | 78.7 | 386 | 73.5 | 93.8 | 6.0 | | |
| Celery | 10 | 318 | 65.6 | 297 | 61.2 | 280 | 57.7 | 88.8 | 7.0 | 5 | 377 | 71.8 | 393 | 74.9 | 377 | 71.8 | 90.6 | 4.9 | 551 | 75.2 |
| | 50 | 352 | 72.6 | 381 | 78.6 | 340 | 70.1 | 94.8 | 6.1 | 10 | 406 | 77.3 | 412 | 78.5 | 405 | 77.1 | 85.2 | 5.7 | | |
| | 100 | 367 | 75.7 | 390 | 80.4 | 347 | 71.5 | 93.3 | 8.0 | 20 | 421 | 80.2 | 435 | 82.9 | 420 | 80.0 | 91.2 | 6.3 | | |

Ave.: average; NP: number of pesticides; PP: proportion of total pesticides spiked.

83.3%; ③ the pesticides currently used in China are mainly of slight toxicity, low toxicity, and medium toxicity, making up 87.2%; ④ high toxicity and extreme toxicity pesticides make up 12.8%; and ⑤ prohibited pesticides, which carry severe safety risks and should be paid more attention to, make up 6.2%. There were 155 pesticides that were only detected by LC-Q-TOFMS, 218 pesticides that were only detected by GC-Q-TOFMS, and 160 pesticides that were co-detected by both GC-Q-TOFMS and LC-Q-TOFMS. For the pesticides detected by only GC-Q-TOFMS or LC-Q-TOFMS, respectively, plus the co-detected

160 pesticides, the detection capability was as follows: 315 pesticides for LC-Q-TOFMS, 378 pesticides for GC-Q-TOFMS, and 533 pesticides for the combination technique. The detection capability increased by 41% for LC-Q-TOFMS and by 29% for GC-Q-TOFMS.

The preliminary findings provide valuable information on the status of pesticide residue in the fruits and vegetables across 31 provinces/municipalities. They also provide information on the regularity of Chinese pesticide applications in fruits and vegetables.

Table 5

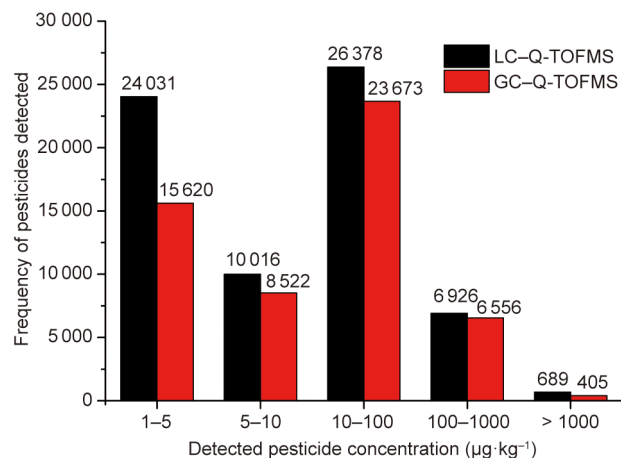
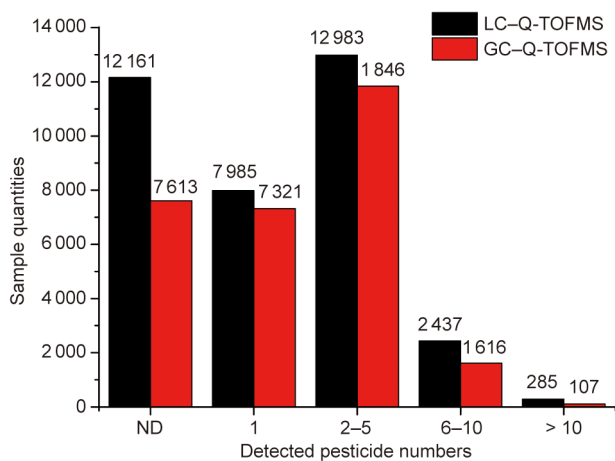
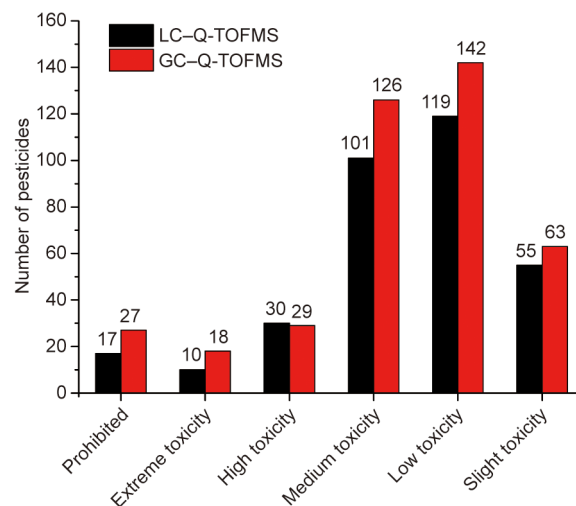
Category and toxicity of the 533 pesticides detected by GC-Q-TOFMS and LC-Q-TOFMS.

| Classification | | LC-Q-TOFMS + GC-Q-TOFMS | LC-Q-TOFMS | GC-Q-TOFMS | Only LC-Q-TOFMS | Only GC-Q-TOFMS | Both |
|------------------|------------------------|-------------------------|------------|------------|-----------------|-----------------|------|
| Function | Insecticide | 225 | 121 | 159 | 66 | 104 | 55 |
| | Herbicide | 151 | 85 | 114 | 37 | 66 | 48 |
| | Fungicide | 129 | 89 | 86 | 43 | 40 | 46 |
| | Plant growth regulator | 16 | 12 | 9 | 7 | 4 | 5 |
| | Others | 12 | 8 | 10 | 2 | 4 | 6 |
| Composition | Organonitrogen | 239 | 171 | 159 | 80 | 68 | 91 |
| | Organophosphorus | 80 | 54 | 54 | 26 | 26 | 28 |
| | Organochlorine | 64 | 10 | 62 | 2 | 54 | 8 |
| | Carbamates | 40 | 27 | 28 | 12 | 13 | 15 |
| | Pyrethroids | 21 | 4 | 21 | 0 | 17 | 4 |
| | Organosulfur | 20 | 12 | 12 | 8 | 8 | 4 |
| | Others | 69 | 37 | 42 | 27 | 32 | 10 |
| Toxicity | Slight toxicity | 91 | 55 | 63 | 28 | 36 | 27 |
| | Low toxicity | 207 | 119 | 142 | 65 | 88 | 54 |
| | Medium toxicity | 167 | 101 | 126 | 41 | 66 | 60 |
| | High toxicity | 46 | 30 | 29 | 17 | 16 | 13 |
| | Extreme toxicity | 22 | 10 | 18 | 4 | 12 | 6 |
| Prohibited | 33 | 17 | 27 | 6 | 16 | 11 | |
| Total pesticides | 533 | 315 | 378 | 155 | 218 | 160 | |

(1) Among the samples analyzed, 56.2% (LC-Q-TOFMS) and 52.4% (GC-Q-TOFMS) of the samples showed no pesticides or only one pesticide residue detected. About 40% of the samples showed 2–5 pesticides detected (Fig. 5).

(2) Pesticides were detected by LC-Q-TOFMS 68 040 times, and by GC-Q-TOFMS 54 776 times, for a total of 115 891 times (excluding duplicate pesticides that were detected by both detectors), as shown in Fig. 6. For 50% (LC-Q-TOFMS) and 44.1% (GC-Q-TOFMS) of the samples, the detection frequencies of the residual levels were lower than the uniform standard of $10 \mu\text{g}\cdot\text{kg}^{-1}$. The test results show that the pesticides detected in Chinese market fruits and vegetables were mainly at low and medium residual levels.

(3) The pesticide residues detected in the investigation were mainly of medium, low, and slight toxicity, as shown in Fig. 7. The detected percentage of pesticides of medium, low, and slight toxicity was 87.4% by LC-Q-TOFMS and 87.6% by GC-Q-TOFMS. This finding demonstrates the consistency of the GC-Q-TOFMS and LC-Q-TOFMS results.

**Fig. 6.** Frequency of pesticides detected for different pesticide concentrations.**Fig. 5.** Sample quantities for different detected pesticide numbers. ND: no pesticides.**Fig. 7.** Classification of the 533 pesticides by toxicity.

(4) The 533 pesticides detected by GC-Q-TOFMS and LC-Q-TOFMS were classified according to function, as shown in Fig. 8. For herbicides, GC-Q-TOFMS is more suitable for detection than LC-Q-TOFMS. The complementarity of these two technologies not only improves the capability to detect unknown risks, but also draws a detailed profile of the status of pesticide residues in the fruits and vegetables on the Chinese market.

(5) In Fig. 9, the 533 pesticides detected by GC-Q-TOFMS and LC-Q-TOFMS are classified according to chemical composition.

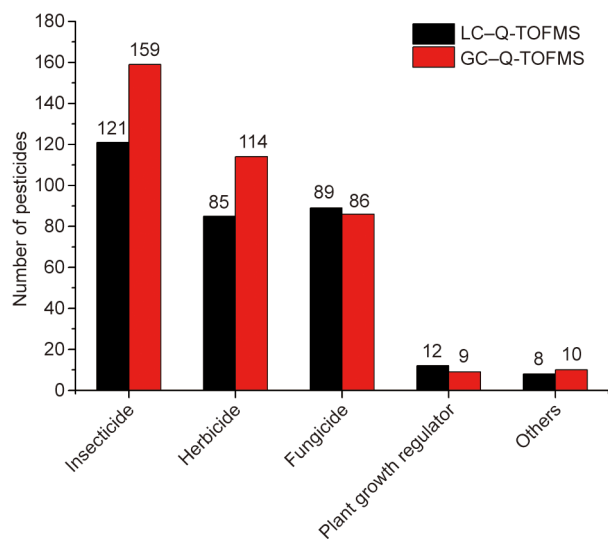


Fig. 8. Classification of the 533 pesticides by function.

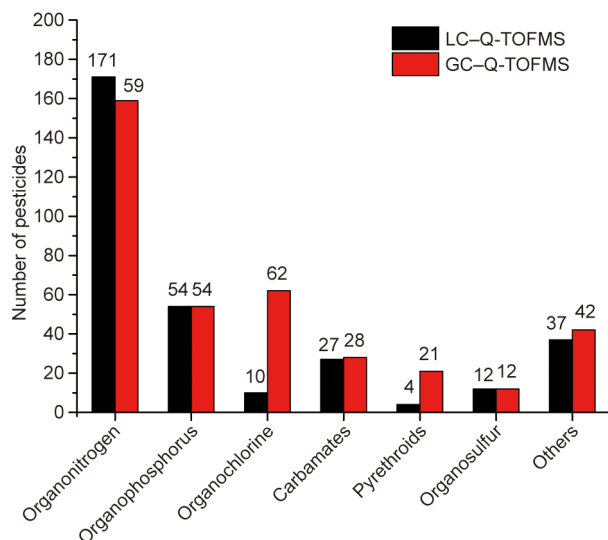


Fig. 9. Classification of the 533 pesticides by composition.

This figure further demonstrates that GC-Q-TOFMS and LC-Q-TOFMS have unique detection features and complement each other. The combination technique can clearly describe the overall comprehensive status of pesticide residues in fruits and vegetables, while using a single technique may risk a partial result.

(6) With the combination technique, the investigation compliance rate was greater than 96.5% according to the MRL standard of China. However, the investigation compliance rate reached only 58.7% and 63.2%, respectively, according to the MRL standards of the Europe and Japan. This comparison indicates that the MRL standard of China is relatively low. In comparison with other countries, there is a large difference in food safety levels (Table 6).

4. Conclusion

In this study, a high-throughput, high-resolution, and non-targeted screening method for the determination of 733 pesticide multi-residues in fruits and vegetables that combines the GC-Q-TOFMS and LC-Q-TOFMS technologies with one sample preparation was studied. This method is based on accurate mass databases developed for 485 pesticides by GC-Q-TOFMS and 525 pesticides by LC-Q-TOFMS, and combines the screening of pesticides in both fruits and vegetables. Data were collected and compared with the accurate mass databases; automatic qualitative identification for pesticides was then introduced. This method also realizes an electronic standard in order to replace the conventional qualitative confirmation method with standard materials as references.

The combination technique possesses the unique advantages of both GC-Q-TOFMS and LC-Q-TOFMS. Furthermore, it merges their complimentary advantages, resulting in the simultaneous detection of 733 pesticides by the combination technique. The number of detectable pesticides and sensitivity of the combination technique was significantly greater than those of GC-Q-TOFMS or LC-Q-TOFMS alone; there were over 488 pesticides with Res. = 60%–120% and RSD < 20% at the 10 $\mu\text{g}\cdot\text{kg}^{-1}$ spiked level with the combination technique in eight different matrices. This method was successfully utilized in the investigation of pesticide residues in 38 138 batched samples covering 18 categories and 134 types of fruits and vegetables in China. The results revealed several features of pesticide application in fruits and vegetables in China. The successful application of the combination technique with agricultural food samples demonstrated that the developed method can not only be used as a new and effective tool for pesticide residue screening, but will also play a very important role in food safety supervision.

Acknowledgements

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Table 6

Comparison of detected pesticides by two techniques for the Chinese, Europe, and Japanese MRLs.

| | LC-Q-TOFMS | | | | | | GC-Q-TOFMS | | | | | |
|--------|------------|----------------|-------|----------------|-------|----------------|------------|----------------|-------|----------------|-------|----------------|
| | ND | Proportion (%) | ≤ MRL | Proportion (%) | > MRL | Proportion (%) | ND | Proportion (%) | ≤ MRL | Proportion (%) | > MRL | Proportion (%) |
| China | 3652 | 29.1 | 8533 | 68.0 | 366 | 2.9 | 2370 | 24.1 | 7165 | 73.0 | 282 | 2.9 |
| Europe | 3652 | 29.1 | 7116 | 56.7 | 1783 | 14.2 | 2370 | 24.1 | 4753 | 58.4 | 2694 | 17.4 |
| Japan | 3652 | 29.1 | 7037 | 56.1 | 1862 | 14.8 | 2370 | 24.1 | 4211 | 55.9 | 3236 | 20.0 |

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Compliance with ethics guidelines

Guofang Pang, Qiaoying Chang, Ruobin Bai, Chunlin Fan, Zijuan Zhang, Hongyuan Yan, and Xingqiang Wu declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eng.2019.08.008>.

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