Research Progress on Detection Techniques of Fungicide Residues in Chinese Chives

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Abstract Chinese chive is a kind of medicinal and edible plant, with many diseases, and chemical fungicides are usually used for control. In order to find out the risk of pesticide residues in Chinese chives, this paper summarized relevant literatures published in recent years, and sorted out and analyzed the types of pesticides used and detection techniques of common diseases in Chinese chives.

Key words Chinese chive; Pesticide residues; Fungicide; Detection technique
DOI:10.19759/j.cnki.2164 -4993.2024.01.011

Chinese chive is a perennial root plant of *Allium* in the Liliaceae family, as well as a unique vegetable variety in China[1]. According to the statistics of the Ministry of Agriculture and Rural Affairs and the investigation and summary of the National Vegetable Industry Technology System, the planting area of Chinese chive in China is about 400 000 hm^2 all the year round, and it is the most widely distributed species among all vegetables[2]. Chinese chives are rich in nutrients and have certain medicinal value. They are rich in vitamins, cellulose, carbohydrates, *etc.*, and thus beneficial for moistening the intestines, promoting bowel movement, regulating qi and blood circulation. Chinese chives are deeply loved by consumers[3]. In the production, circulation, and storage process of chives, common diseases include gray mold, blight, wilt, rust, powdery mildew, yellow leaf disease, dry tip, southern blight, stem wilt, soft rot, and other fungal diseases, which can seriously reduce yield and quality. Organic fungicides are often used, that is, chemical substances are used to inhibit or kill bacteria, fungi and other microorganisms to ensure their yield and quality[4]. Organic fungicides have a wide range of activity and multiple action sites, making them an effective means to reduce the decay and disease of Chinese chives. They are also widely used as preservation measures during circulation and storage[5]. Fungicides have played a vital role in protecting the growth, increasing the yield and ensuring the storage quality of Chinese chives, but the residue of fungicides will inevitably pollute Chinese chives, which will have a negative impact on animal and human health. In recent years, the public announcement of food safety sampling results in China has frequently exposed the problem of fungicide pollution in Chinese chives, which is mainly caused by the fungicide procymidone exceeding the standard[6-7], which has caused consumers to know "poisonous Chinese chives".

The problem of fungicide residues is highly concerned by the society[8], and there are more than a thousand standards related to agrochemical safety and limits issued and implemented by various countries and regions respectively. The implementation of a series of laws and regulations in China has also strengthened the supervision of agrochemicals, such as the *Food Safety Law of People's Republic of China* (PRC), the *Quality and Safety Law of Agricultural Products of People's Republic of China* (PRC), and the *Regulations of the People's Republic of China on Pesticide Management*. The current national standard GB 2763-2021 *National Food Safety Standard—Maximum Residue Limits for Pesticides in Food* stipulates the maximum residue limits (MRL) of nearly 160 fungicides[9].

General Situation of Common Fungicides in Chinese Chives

Fungicides usually refer to chemical agents that can effectively prevent and kill pathogenic microorganisms, and can be divided into systemic fungicides and protective fungicides according to

Received: October 20, 2023 Accepted: December 23, 2023
Supported by Special Project of the Central Government in Guidance of Local Science and Technology Development (Scientific and Technological Innovation Base Project) (226Z5504G); The Fourth Batch of High-end Talent Project in Hebei Province.
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different modes of action. Systemic fungicides can be absorbed into plants by leaves, stems, roots and seeds, and have therapeutic and protective effects, such as carbendazim and metalaxyl. Protective fungicides can't be absorbed, conducted and preserved by plants, and can't be used to prevent and treat diseases that go deep into plants, but only have protective effects, such as mancozeb, thiram and chlorothalonil[10]. Common fungicides used in Chinese chives are procymidone, pyrimethanil, dimethomorph, iprodione and so on.

Pretreatment Techniques of Common Fungicides in Chinese Chives

The matrix of Chinese chives is very complex, and sample pretreatment techniques are particularly critical for the detection of fungicide residues in Chinese chives. It is not easy for traditional sample pretreatment techniques to achieve effective purification of matrix components, and matrix effect is easily produced on pesticide detection and leads to a great impact on the sensitivity of analytical instruments, thus affecting the accuracy and reproducibility of the determination results[11]. At present, the pretreatment techniques are developing towards time-saving, labor-saving, high efficiency, less reagent consumption and less environmental impact. Commonly used pretreatment methods include solid-phase extraction (SPE), solid-phase microextraction (SPME), dispersive solid-phase extraction, liquid-liquid extraction, gel permeation chromatography (GPC) and QuEChERS method[12].

Solid-phase extraction

Solid-phase extraction (SPE) is a pretreatment technique developed in recent years, and its principle is to use the separation principle of liquid chromatography (LC). First, solid adsorbents are used to selectively adsorb pesticide components and remove sample matrix and interfering compounds, and eluents are then used to elute pesticides[13]. This technique reduces sample pretreatment processes, has simple operation, high recovery and good reproducibility, and can be combined with other instruments to realize automation. It is more and more widely used in the detection of fungicide residues. However, most solid-phase extraction columns are disposable, and although the purification effect is good, the cost is high when the sample dosage is large, and the concentration process takes a long time[14].

Zhang *et al.*[15] purified the acetonitrile extract of a Chinese chive sample by a graphitized carbon black/amino mixed solid-phase extraction columns, eluted it and concentrated it to constant volume for detection. The recovery values of cypermethrin were between 81.7% and 99.1%, and the relative standard deviation (*RSD*) values were between 2.5% and 8.7%. The detection limit and quantitative limit of this method were 0.001 and 0.01 mg/kg, respectively, which could meet the requirements for the detection of cypermethrin residues in Chinese chives. Xi *et al.*[16] used an Oasis MCX solid-phase extraction column to extract and purify samples, and detect 13 fungicides in the samples combining with ultra pressure liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). The recoveries were in the range of 80% – 101%, and the detection limit was 0.1 – 1.0 g/L. Xu *et al.*[17] used an acetonitrile homogenization method for extraction and a solid-phase extraction column for the treatment of vegetable samples. The average recoveries of dichlorvos and benzoyl urea fungicide residues were between 83.5% and 105.6%, and the method was suitable for the detection of pesticide residues of the above two fungicides in vegetables. Zhou *et al.*[18] established a UPLC-MS/MS method for the simultaneous determination of six strobilurin fungicides residues by an amino solid-phase extraction pretreatment and purification technique. The method is simple to operate and can meet the detection requirements of six strobilurin fungicide residues in fruits and vegetables with good repeatability.

Solid-phase microextraction

Solid-phase microextraction (SPME) is a new sample pretreatment technique, which integrates extraction, concentration and injection, and was developed on the basis of the solid phase extraction technique in the early 1990s. According to different extraction methods and extraction devices, it can be combined with various detection techniques, and has the obvious advantages of simple operation, time saving, safety, high sensitivity, good selectivity, no need for solvent and so on. SPME relies on extraction fiber instead of fillers to separate targets, and the extraction fiber can be reused, so it is no longer a disposable consumable. However, because the use of SPME needs special equipment, it can only be used for a small number of pesticide residues, and although the materials can be reused, the required equipment is expensive and the cost is still high, which leads to the fact that SPME is not as widely used as SPE in pesticide residue detection and analysis at present[19]. Liu *et al.*[20] used solid-phase microextraction for pretreatment, and detected 23 residues of organophosphorus pesticides and pyrethroids in vegetables. Munitz *et al.*[21] studied the determination of azoxystrobin and pyraclostrobin residues in blueberries by a solid-phase microextraction pretreatment method, which has good selectivity, accuracy and sensitivity. Cui[22] used an optimized solid-phase microextraction method to detect 161 pesticide residues. A solid-phase microextraction device was added to a headspace vial of the internal standard sample, and SPME fiber was added and extended out of the extraction head. After that, the extraction fiber was detected, and the average recoveries were in the range of 60.0% – 110.0%. The method has good repeatability, indicating that the solid-phase microextraction method has good treatment effect.

Liquid-liquid extraction

Liquid-liquid extraction (LLE) is a traditional pretreatment technique for early agricultural products, which is often used to detect fungicide residues. It is conducted mainly depending on different solubility of pesticides in different solvents, and has the advantages of simplicity and high extraction efficiency. Extraction solvents used in the operation process of this method include ethyl acetate and dichloromethane, formic acid and methanol, acetonitrile, acetone, *etc.* Most testing institutions in China still use the pre-treatment methods for detecting residues of organophosphorus and organochlorine pesticides in national food safety standard, *Pesticide Multiresidue Screen Method for Determination of Organophosphorus Pesticides, Organochlorine Pesticides, Pyrethroid Pesticides and Carbamate Pesticides in Vegetables and Fruits* (NY/T 761-2008), and acetonitrile is used to extract pesticides and their metabolites from Chinese chives to confirm pesticide residues such as fungicides in Chinese chives[23]. The treatment method has high extraction efficiency and short treatment time, but the purification method of the pretreatment method has some shortcomings, especially the shortcomings of too-high salt content in extracting solutions, excessive pigment residue and complex matrix, which easily affect the detection by instruments. Liquid-liquid extraction can better complete the extraction and purification of pesticide residues if it is combined with other conditions or techniques. Some studies have used low-temperature enrichment liquid-liquid extraction combined with gas chromatography-tandem mass spectrometry to detect 15 pesticide residues in samples, and the results also meet the requirements of relevant standards[24]. It has been fully proved that liquid-liquid extraction combined with low temperature can meet the requirements of pesticide residue detection in agricultural products more effectively.

Gel permeation chromatography

Gel permeation chromatography (GPC) separation is a physical process, which is widely used in the analysis of organic pollutants. It can well separate organic macromolecules, and has the advantages of wide application range, good reproducibility, column reuse and high degree of automation. However, for samples with complex matrix, it is difficult to remove impurities with similar molecular sizes by gel permeation chromatography, and large amounts of organic solvents are needed when using GPC columns with large inner diameters, which are difficult to operate. GPC has a good purification effect on samples such as Chinese chives with a high content of pigments, as it effectively reduces matrix interference and improves the pretreatment efficiency of fungicide residues.

Liu *et al.*[25] extracted Chinese chive samples by acetonitrile, and purified the extract by GPC, and an ultra-inert liner was selected for the inlet, which could significantly reduce the matrix effect of strong polar pesticides such as methamidophos, acephate, omethoate and isocarbophos. Feng *et al.*[26] used GPC combined with gas chromatography-mass spectrometry (GC-MS) to detect 41 pesticide residues in fruits and vegetables. The samples were extracted with acetonitrile-sodium acetate buffer, and the average recoveries ranged from 71.0% to 125.4%. The purification effect and accuracy of the method met the detection requirements.

QuEChERS techniques

Quechers (quick easy cheap effective rugged safe) is a sample pretreatment technique based on dispersive solid-phase extraction, which was first proposed by American scientist Lehotay *et al.* in 2002. Its technical principle is similar to that of solid-phase extraction, which uses the interaction between adsorbent fillers and impurities in the matrix to adsorb impurities, so as to achieve the purpose of impurity removal and purification. In 2018, the publication of *National Food Safety Standard, Determination of 208 Pesticides and Metabolites Residues in Food of Plant Origin: Gas Chromatography-Tandem Mass Spectrometry* (GB 23200.113-2018), marked that the QuEChERS technique officially entered the ranks of Chinese standard detection methods. This standard adopts the QuEChERS pre-treatment method, which can simultaneously detect 208 pesticide residues in one needle. The pre-treatment process is simple and efficient, and the recovery is good, basically above 80%[16]. Compared with SPE, QuEChERS is more in line with the current situation of pesticide residue detection in agricultural products. The emergence of QuEChERS has a significant impact on pre-treatment processes, and many optimization methods based on the QuEChERS technique have emerged, including changing pH values, changing salt formulations, and changing solvents. These methods have significant advantages such as simplicity, efficiency, speed, safety, and low cost, and have been widely used in the detection, analysis, and rapid screening of pesticide residues in Chinese chives[27-28].

Luo[29] established a method for detecting 60 pesticide residues in Chinese chives based on QuEChERS-GC-MS/MS by using liquid nitrogen cryogenic crushed samples and adding analyte protectants. The new method had lower matrix effect and eliminated the need for processing blank matrixes. The sensitivity, accuracy, precision, standard curve and linear range of the method all met the analysis requirements. It has advantages in sample preparation, high-throughput detection, and accurate quantification. Zhong *et al.*[30] used a QuEChERS method for pre-treatment of chive samples, combined with GC-MS/MS for detection and the external standard method for quantification. The results showed that the linear relation of the six pesticides, including carbendazim and carbendazim, was good within corresponding ranges, with correlation coefficients above 0.99. The recoveries of the six pesticides were in the range of 87.3% – 112.8%, and the relative standard deviations were in the range of 7.6% – 16.8%. It indicates that the method is sensitive, efficient, and accurate, and suitable for the rapid detection of most pesticide residues in Chinese chives.

Detection and Analysis Methods of Common Fungicide Residues in Chinese Chives

With the improvement of modern analytical chemistry technology, the popularization of mass spectrometry and the rapid development of other pretreatment techniques, MS is widely used in the detection of pesticide residues. GC, GC-MS/MS, LC, LC-MS/MS and immunoassay are mainly used to detect fungicide residues in Chinese chives.

Gas chromatography

GC uses gas as the mobile phase to separate and determine samples through a chromatographic column filled with fillers. It has the characteristics of simple operation, high selectivity, good separation efficiency, high sensitivity and low detection limit. GC can be used to detect fungicides that are volatile and will not decompose, and can achieve the effect of one sample injection and complete separation of components to be detected. It is one of the most commonly used methods for pesticide residue detection at present. However, there are also some shortcomings, such as difficulties in analyzing thermally-unstable pesticide components and false positive or false negative results caused by interference in complex matrices.

Wang *et al.* [31] used QuEChERS pretreatment and GC to establish a detection method for 16 pesticide residues in 4 kinds of fruits and vegetables. Through the methodological evaluation of samples with a high pigment content and complex matrix, it was found that the linearity of each component was good in the range of 2.0 – 100 μg/L, the average recoveries of samples were in the range of 70.1% – 119.0%, and the *RSD* values were in the range of 0.23% – 5.2%. The method is simple, rapid, accurate and efficient, and can be used for rapid screening and quantitative detection of organochlorine residues in vegetables and fruits. Hong *et al.* [32] established a method for the determination of 16 organophosphorus pesticide residues in Chinese chives by GC. The recoveries of the method were between 77.0% and 107.0%, and the relative standard deviation (*RSD*) values were between 1.3% and 3.2%. The method has the characteristics of less solvent consumption, simple operation and high efficiency.

Gas chromatography-tandem mass spectrometry

GC-MS/MS is to combine the high-efficiency separation ability of a gas chromatograph with the unique selectivity, sensitivity, relative molecular weight and molecular structure identification ability of a mass spectrometer by connecting the gas chromatograph and the mass spectrometer in series, so as to achieve the purpose of qualitative and quantitative detection of analytes. GC-MS/MS has been widely used in the detection of pesticide residues, especially in the detection of pesticide metabolites, degradation products and multi-pesticide residues.

Zhang *et al.* [33] extracted Chinese chive samples with acetonitrile, purified the extracts with graphitized carbon black/ammo column (PC/NH2), detected the purified samples by GC-MS/MS in the selective ion monitoring scanning mode (SIM), and performed quantification by a matrix-matched solution external standard method. The results showed that the targets showed a good linear correlation in the range of 65.2 – 1 043.0 ng/ml. He *et al.* [34] combined QuEChERS pretreatment with GC-MS/MS to detect 213 pesticide residues in Chinese chives, and used commercial extraction salt packages and dispersive solid-phase extraction adsorbent packages to simplify the extraction procedure. The detection limits of most pesticides were 2 μg/kg; the correlation coefficient R^2 values were greater than 0.99; and the average recoveries were in the range of 70.0% – 120.0%, and the relative standard deviations were less than 20%. The accuracy and sensitivity of the method are in line with the detection of pesticide residues in Chinese chives. Zhu *et al.* [35] adopted a QuEChERS rapid pretreatment method for purification and determined the test solutions by GC-MS/MS. A triple quadrupole gas chromatography-mass spectrometry method for the determination of chlorothalonil and other 51 pesticide residues in Chinese chives was established, and the multi-reaction monitoring mode was used for qualitative confirmation and quantitative analysis, which improved the sensitivity of the method and obtained a low detection limit.

Liquid chromatography

LC was developed in 1970s in combination with some limitations of GC. It is especially suitable for the detection and analysis of ionic and macromolecular compounds with high boiling points, poor thermal stability and strong polarity. In the analysis of samples, it has the characteristics of fast flow rate of carrier liquid, repeated use of chromatographic column, no damage to samples and easy recovery. It has become an indispensable and important method for the detection of organic fungicide residues.

Wang *et al.* [36] established an HPLC method for the simultaneous determination of carbendazim, imidacloprid and other seven pesticide residues in Chinese chives and scallions. Samples were extracted using acetonitrile, purified by an amino solid-phase extraction column, detected by an ultraviolet detector and quantified by the external standard method. The results showed that in the range of 0.03 – 4.0 mg/L, the linear correlation coefficients of 7 pesticides were all greater than 0.99, and the detection limits were 0.006 – 0.05 mg/kg. Yu *et al.* [37] proposed a method for simultaneous determination of 10 kinds of antiseptic fungicides in fruits and vegetables by HPLC, and the detection limits of these 10 kinds of antiseptic fungicides were between 0.02 and 0.05 mg/L. It provides a reference for future research on screening and confirmation, risk assessment and quantitative arbitration of pesticide residues in vegetables in the field of food risk monitoring.

Liquid chromatography-tandem mass spectrometry

LC-MS/MS is a method that connects a liquid chromatograph with a mass spectrometer, separates substances to be detected by LC, and then analyzes and detects the mass fragments of separated ions of the detected substances by MS. It is used to analyze compounds with poor thermal stability, large molecular weights and low concentration, which are difficult to be analyzed by GC. LC-MS/MS has the obvious advantage of multi-residue detection and analysis. LC-MS/MS is a highly efficient and reliable analytical technique for pesticide residues, which has the advantages of high detection sensitivity, good selectivity, and simultaneous qualitative and quantitative analysis, and can provide relative molecular weight and structural information of components to be detected.

Sun *et al.* [38] established a method for simultaneous determination of 100 pesticide residues in Chinese chive samples by UPLC-MS/MS combined with QuEChERS pretreatment. The average recoveries were in the range of 71.1% – 115.6%, and the *RSD* values were in the range of 0.6% – 17.0%. The method was efficient and stable, and suitable for rapid detection and screening of pesticide residues in Chinese chives. Huang *et al.* [39] established a method for the determination of 12 organophosphorus pesticide residues in Chinese chives by LC-MS/MS. The samples were extracted by acetonitrile, purified by solid-phase extraction column, separated by a C18 column, scanned by electrospray positive ion source (ESI+) and determined in the multi-reaction monitoring mode (MRM). The detection limits were in the range of 0.02 – 0.6 μg/kg, which met the detection requirements.

Immunoassay

Immunoassay is an analytical method based on the principle of specific binding of antigens and antibodies. Specific pesticide residues in samples can be qualitatively and quantitatively detected by labeling haptens or antibodies, through biological, physical or chemical amplification of labels. Immunoassay has many advantages, such as strong specificity, high sensitivity, simple operation, and high-throughput determination. It does not need expensive instruments and can simplify the pretreatment process. At present, it is mostly used for rapid qualitative screening of pesticide residues.

Liu *et al.* [40] established a direct competitive enzyme-linked immunosorbent assay (ELISA) method based on polyclonal antibodies against carbendazim for the detection of carbendazim residues in fruits and vegetables. The detection limit of the calibration curve of the method was (0.30 ± 0.15) μg/L, and the sensitivity was (2.70 ± 0.30) μg/L. Ni[41] established a detection method of procymidone residues in Chinese chives with monoclonal antibodies, which had good linearity, and a colloidal gold immunochromatographic test strip was prepared. The minimum limit of the test strip for detecting procymidone in Chinese chives was 1 μg/kg, which had high sensitivity.

Conclusions

As a very important part of analytical work, the pretreatment techniques of organic fungicides are developing continuously, and solid-phase extraction and the QuEChERS method among them are more and more widely used in the sample pretreatment step of pesticide residue detection for their superior reproducibility, accuracy and efficiency. Solid-phase extraction has a good purification effect, but it has the disadvantages of high material cost, complicated operation and low efficiency. The QuEChERS technique has the advantages of high recovery, wide versatility, less solvent consumption, environmental protection and high throughout, but it also has some problems such as poor purification effect, obvious matrix effect and low sensitivity. Follow-up research should continue in the direction of rapidity, simplicity, energy saving, environmental protection, high accuracy and high throughout. In the detection and analysis of fungicides, chromatography combined with MS has become an important method for pesticide residue detection[41]. The detection method has high sensitivity, good selectivity and accurate qualitative and quantitative analysis. Although it requires high equipment and is not suitable for on-site detection, it is still a widely-used, efficient and reliable pesticide residue analysis technique.

Chinese chive is a kind of bulb vegetable, which contains sulfur compounds and high pigment content. Its sulfide properties are similar to those of pesticides, and it is easy to be extracted together with pesticides, which interferes with analysis and determination. When establishing detection methods, not only should the properties of target substances be considered, but also the characteristics of samples should be taken into account. Existing pretreatment techniques for pesticide residue detection is immature or limited in effective materials, so they have shortcomings in practical application. In order to improve the extraction efficiency of pesticide residues in Chinese chives and reduce the matrix effect, sample pretreatment should be developed in following two directions: ① to explore the functional research of pretreatment materials and improve their extraction ability and selectivity, and ② to increase the extraction form to improve the pretreatment efficiency. With the development of science and technology, scholars are actively exploring various efficient and advanced pretreatment methods and constantly developing new detection techniques to meet the urgent needs of pesticide residue detection and production safety of agricultural products.

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Editor: Yingzhi GUANG Proofreader: Xinxiu ZHU