Application of Mass Spectrometry (MS)-coupled Techniques in Pesticide Residue Detection

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Abstract Pesticide residue detection is an important work to ensure the quality safety of agricultural products. In the process of agricultural production, in order to prevent and control agricultural diseases and pests, a certain amount of pesticides need to be used. However, if pesticides are used excessively, there will be certain pesticide residues in crops and related products. Therefore, it is necessary to do a good job in pesticide residue detection. The gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) detection methods have good results and can effectively detect pesticide residues in related products. This paper reviewed and analyzed the application of GC-MS and LC-MS in pesticide residue detection, and proposed optimization measures based on practical experience, hoping to provide reference for relevant scholars.

Key words Gas chromatography-mass spectrometry; Liquid chromatography-mass spectrometry; Pesticide residues; Detection analysis; Application

DOI:10.19759/j.cnki.2164-4993.2023.05.014

Due to various types of pesticides that may remain in agricultural products during production, significant differences in chemical structures and interference from other impurities, it is necessary to establish sensitive, accurate and efficient detection methods. At present, the analysis and detection methods for pesticides include chemical analysis, thin layer chromatography (TLC), high-performance liquid chromatography (HPLC), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), *etc.* [1-3].

Based on the development and improvement of MS-coupled techniques, liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography-mass spectrometry (GC-MS) techniques are currently considered the most accurate methods for quantitative analysis of analyzed compounds[4], playing a significant role in compound identification and detection in the laboratory. In pre-treatment, MS-coupled techniques have the characteristics of complementary advantages, simple sample processing, and reduced pressure of sample pre-treatment, making it suitable for the analysis of complex matrix samples. In terms of qualitative and quantitative analysis of compounds, they have high sensitivity, fast analysis speed, and outstanding specificity, and are suitable for precise quantification of multiple components[5]. They can obtain rich information, and the quantitative and qualitative results are reliable, fast and simple, and highly automated, and the recovery is high. Sun[6] has studied the application of LC-MS in the detection of pesticide residues in tea. Research has shown that LC-MS has shown simple and fast characteristics in determining three types of pesticide residues, including organophosphorus pesticide residues and phenoxycarboxylic acid herbicide residues, and the recovery and precision are also within the requirements of pesticide residue analysis standards. Pei[7] has studied the rapid determination of trace components in drugs using LC-MS, showing that the LC-MS technique can quickly, sensitively and accurately analyze trace components in drugs. Above studies have highlighted the advantages of LC-MS, but there is limited introduction to GC-MS. This paper comprehensively analyzed the application of GC-MS and LC-MS in pesticide residue detection, and proposed optimization measures for their shortcomings combining with practical experience, hoping to provide reference for relevant researchers.

Analysis on Basic Concepts and Advantages of GC-MS and LC-MS

Analysis on basic concepts and advantages of GC-MS

GC has good separation ability, but its qualitative analysis ability for unknown compounds is poor. MS has good detection ability for unknown compounds and high detection sensitivity, but this technique requires the detected components to be pure compounds. Combining gas chromatography with mass spectrometry techniques allows them to complement each other, which not only solves the problem of difficult detection of unknown components in complex compounds by GC according to retention time, but also

Received: June 25, 2023 Accepted: August 27, 2023

Supported by The Fourth Batch of High-end Talent Project in Hebei Province; Tangshan Science and Technology Entrepreneurship and Innovation Leading Talent Project (21130243A); Special Project of the Central Government in Guidance of Local Science and Technology Development (226Z5504G); Tangshan Talent Project (A202202005).

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uses a mass spectrometer with strong detection ability and high sensitivity as the detection equipment, which based on its good resolution and sensitivity and good application effects in fields such as medicine and pesticides, is an effective tool for separating and detecting complex compounds[8].

GC-MS has following advantages: ① GC-MS has good separation effect. Based on gas chromatography separation as the basic principle, combined with the specificity advantages of mass spectrometry, GC-MS can analyze complex detection objects with efficient separation effects. ② The GC-MS detection technique can achieve the analysis of unknown substances. Corresponding detection instruments are employed to compare and analyze ionized ion fragments, which are searched in the spectrum library, and similarity comparison analysis is performed based on the composition of ion fragments, so that similar known substances can be retrieved and unknown substances can be determined.

Analysis on basic concepts and advantages of LC-MS

LC-MS is a detection technique that uses a liquid chromatograph equipment as the separation system and a mass spectrometer as the detection system. Samples are separated in the mobile phase of the LC separation system, and after ionization treatment, the ion fragments can be separated by mass using a mass analyzer of MS. After passing through a detector, a mass spectrum can be obtained. LC-MS demonstrates the complementary advantages of chromatography and mass spectrometry, including the separation ability of chromatography for complex detection objects and the high selectivity and sensitivity of mass spectrometry detection. It plays an important role in fields such as drug detection and food analysis[9].

The LC-MS detection technique has following advantages: ① The LC-MS detection technique has high sensitivity and strong specificity. In specific application processes, the mass spectrometer equipment is used to record ions as signal targets, which can quickly respond to the detection of target substances, and the detection limit is low. The selection conditions for different ions are different, so the detection has significant specificity. ② The LC-MS detection technique has high efficiency. Rapid separation can be achieved at low separation rates by using a mass spectrometer to screen and detect ions and analyzing them under the same chromatographic condition[10].

Specific Application of GC-MS in Pesticide Residue Detection

GC-MS is a detection method that combines GC and MS, of which MS has high detection sensitivity and strong qualitative analysis ability, and GC has strong separation ability and can achieve quantitative analysis. Combining them for application can effectively improve the detection effect. The GC-MS technique has strict requirements for the preliminary treatment of tested samples, with the main purpose of purifying tested substances in the samples, maximizing the elimination of impurities in sample matrixes, and thus avoiding interference with determination. In the process of extracting fruit and vegetable products, the composition of the extracts is relatively complex. When organic solvents are used to extract pesticide residues in samples, oil, wax, protein, and chlorophyll in the samples will be extracted together with pesticide residues, resulting in a large amount of impurities in the extracts that interfere with pesticide residue detection. Therefore, solid-phase extraction pretreatment is necessary[11]. Wang *et al.*[12] established a method for simultaneous detection of 50 pesticides in yams using the QuEChERS technique combined with GC-MS/MS, and conducted preliminary screening on 30 batches of yams from the market. The results showed that the linear relationships of the 50 pesticide concentrations were good within the range of 0.002 – 0.2 mg/L, with average recovery in the range of 71.2% – 104.1%. Chen *et al.*[13] conducted a solid-phase extraction-GC-MS method for the detection of organochlorine pesticide residues in honeysuckles. The results showed that the average recovery values of 20 organochlorine pesticides in honeysuckles were in the range of 80.2% – 115.4%.

Specific Application of LC-MS in Pesticide Residue Detection

The LC-MS detection technique combines the advantages of the separation ability of LC and the ability of MS in tandem to obtain selected ion fragments. As a sample injector for MS in tandem, LC can separate mixtures through its separation ability into single components, which then enter the ion source of MS in chronological order. In the ion source of MS, the ions generated by ionization have differences in mass-to-charge ratio, and after passing through a quality analysis instrument and reaching the detection instrument of MS, signals are detected and amplified. Due to the good effect of liquid LC on separation and identification of non-volatile and thermally-unstable substances, it can be combined with GC to detect pesticide residues[14]. Zhang *et al.*[15] established an LC-MS/MS detection method for three pesticides, triazophos, isocarbophos, and acetamiprid, in four Chinese herbal medicines: Flos Chrysanthemi, Rhizoma Dioscoreae, Radix Ophiopogonis and Flos Lonicerae, and the mass concentrations showed good linear relationships in the range of 0.001 – 0.500 mg/L.

Analysis on the Application and Development of GC-MS and LC-MS in Pesticide Residue Detection

Pesticide residue detection is an important work to ensure food safety. If pesticide residues are not detected in food, people may experience poisoning and other risks after consuming food containing pesticide residues, which seriously affects people's physical health and life safety. China attaches great importance to the detection of pesticide residues in food and has issued multiple standard and normative documents, clarifying the types and standards of pesticide residues in food, which is of great significance in

ensuring food safety. To clarify the specific situation of pesticide residues in food, it is necessary to detect them. However, due to the heavy workload of food pesticide residue detection, if the efficiency of detection techniques is low, it will lead to extension of detection time and increased detection costs. Meanwhile, if the accuracy of detection techniques cannot be guaranteed, and the detection results will not match actual situation, which will also increase food safety risks. Therefore, it is necessary to strengthen the application of advanced pesticide residue detection techniques. After years of development in China's pesticide residue detection techniques, the detection system of food pesticide residues is becoming more and more perfect, and the level of detection techniques adopted is also constantly improving. The application of GC-MS and LC-MS detection techniques has made China's food safety detection industry step up to a new level[16].

With the detection of agricultural products such as vegetables and fruits as an example, the overall application amount of pesticides during the planting process of vegetables and fruits is relatively high, and vegetables and fruits usually contain multiple types of pesticide residues. Moreover, the varieties are complex and the overall difference is great, so it is impossible to detect them under the same chromatographic conditions. Traditional pesticide residue analysis generally uses selective gas chromatograph detectors, but this detection technique can only detect and analyze one type of pesticide and is not suitable for analyzing multiple residual pesticides. Liu *et al.*[17] established a fully-automated solid-phase extraction-LC-MS detection method for the determination of seven new biopesticides residues in fruits and vegetables, including melatonin, matrine, oxymatrine, nicotine, rotenone, veratrine, and jinggangmycin. Fu *et al.*[18] found that improved QuEChERS combined with GC-MS method for the detection of fenobucarb, quintozene, hexachlorobenzene and heptachlor showed recovery in the range of 87.5% – 109.5%, with relative standard deviations in the range of 0.29% – 4.57%. The introduction of GC-MS and LC-MS technologies to fill gaps in the detection of multiple pesticide residues. The two coupled detection techniques can identify multiple pesticide residues in food through a single detection, realizing qualitative and quantitative analysis of pesticide residues in agricultural products, and achieving good results in practical applications.

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Editor: Yingzhi GUANG Proofreader: Xinxiu ZHU