Research Progress of QuEChERS Pretreatment Technique in the Detection of Multiple Pesticide Residues

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Abstract The QuEChERS extraction technique is a pretreatment technique that has been rapidly applied in recent years and is widely used in the field of pesticide residues with many advantages. This technique is based on solid phase extraction (SPE), which uses the interaction between adsorbent and impurities in the matrix to achieve the purpose of purification. The method has easier operation and better purification effect than SPE. In this paper, the research progress of the QuEChERS technique in pesticide residue detection in different fields in recent years and its future development were reviewed, hoping to provide reference for further development and utilization of the QuEChERS technique in pesticide residue detection in the future.

Key words QuEChERS; Pretreatment; Pesticide residues; Research progress

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Food safety is an important issue that all countries in the world attach great importance to, and the detection of pesticide residues in food is the main content of food quality and safety detection. When detecting pesticide residues in food, it is necessary to pretreat samples to be detected first. There are many traditional sample pretreatment methods, most of which often require a large amount of extractants and a long extraction time, and their purification steps are also very complicated. It is difficult for traditional methods to achieve better extraction and analysis of large quantities of pesticides at the same time, so that the extraction efficiency is relatively low. However, the development of QuEChERS technique has solved this problem. It provides some technical support for food safety supervision. Based on its value, many scholars began to apply and study it. On the basis of previous development, many scholars have continuously studied and improved the QuEChERS method according to the characteristics and functions of different pesticides. The QuEChERS method using a sodium acetate buffer salt system for extraction developed by Lehotay[1] is suitable for the extraction of atrazine, chlorothalonil, chlorpyrifos, dichlorvos and other drugs in grapes, lettuce and oranges. Simin *et al.*[2] used the QuEChERS method using a sodium citrate buffer salt system for extraction to analyze and detect 80 kinds of pesticides in Chinese cabbage, and the recovery of the 80 kinds of target pesticides could reach 78.5% - 111.3%.

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Introduction of QuEChERS Method

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) pretreatment technique is a new sample treatment technique based on the rapid sample treatment technique of matrix solid-phase dispersion (MSPD). From the perspective of principle, the QuEChERS method is similar to solid-phase extraction (SPE), and both of them purify samples through the interaction of adsorbents and various impurities in matrixes, but the QuEChERS method is simpler than SPE. The original purpose of establishing this method is to develop a rapid sample pretreatment technique for detecting agricultural plant products such as fruits and vegetables. Nowadays, the QuEChERS technique has become the global standard sample preparation technique for detecting pesticide residues in vegetables and fruits. In recent years, its development field has been increasingly extensive, involving the detection of meat, blood samples, drugs, deep-processed foods and environmental samples.

It is found that the extractant acetonitrile in the QuEChERS method can be replaced by methyl dipropylene, which can be widely used in GC/NPD, FPD or ECD detection. Compared with traditional methods, the QuEChERS method has following advantages: ① high recovery (the recovery of a large number of polar and volatile pesticides is more than 85%), ② high accuracy (reproducibility less than 5%, corrected by the internal standard method), ③ short analysis time (six pre-weighed samples can be determined within 30 - 40 min), ④ less solvent consumption, less pollution and no chloride-containing solvent, and ⑤ simple operation (it can be completed well without good training and higher skills)[3].

Research Progress in Application of QuEChERS Method in Recent Years

Application of QuEChERS method in detection of pesticide residues in vegetables and fruits

The QuEChERS extraction method was used for the treatment

of fruits and vegetables at the beginning of its establishment, and now its development in this field has basically matured. Ferracane *et al.* [4] applied the QuEChERS extraction method and flow modulation-integrated two-dimensional gas chromatography-triple quadrupole mass spectrometry to determine multiple pesticide residues in tomatoes, cucumbers, sweet red peppers and iceberg lettuce. The results showed that the recovery of pesticide residues in different substrates could reach 53% – 160%, and the coefficients of variation were in the range of 1% – 28%. Yu *et al.* [5] established a method for rapid determination of eight organochlorine pesticides in green leafy vegetables by dispersive liquid-liquid microextraction-GC-MS/MS based on QuEChERS modified by Fe3O4 magnetic nanoparticles (Fe_3O_4-MNPs). The experiment used 1 ml of extract obtained in the QuEChERS process as dispersant and 40 μl of chloroform as extractant, and then, 4 ml of water was added. After mixing evenly, dispersive liquid-liquid microextraction was carried out. The results showed that replacing expensive GCB with carbon black in the experiment would not reduce the recovery efficiency. The recovery in the experiment ranged from 78.6% to 107.7%, and the RSD was not more than 7.5%. The method can be successfully used to detect organic pesticide residues in green leafy vegetables. Tang *et al.* [6] established a UPLC-MS/MS method for simultaneous determination of six pesticides in pak choi. The results showed that the experiment is helpful to determining the maximum amount of residue and is of great significance to evaluate food safety.

Application of QuEChERS method in the detection of pesticide residues in drugs

Huang *et al.* [7] applied QuEChERS combined with GC-MS/MS to detect 63 kinds of agricultural residues in *Lycopus lucidus*. The experimental results showed that the average recovery of each pesticide compound was 71.5% – 120.4% at three addition levels (0.05, 0.25 and 0.75 mg/kg). Five kinds of pesticide residues, including permethrin, propiconazole, isazofos, benalaxyl and trifloxystrobin, were detected in *L. lucidus* from different habitats to varying degrees. Li *et al.* [8] simultaneously detected 74 pesticide residues in *Panax notoginseng* established by the combined application of the QuEChERS technique and GC-MS/MS, so as to analyze the data of 20 batches of *P. notoginseng* samples in the market. The average recovery was controlled between 70% and 120%, and the RDS was less than 20%. The results showed that nine pesticides were detected, and quinene exceeded foreign standards. This method can be successfully applied to the detection of pesticide residues in 20 samples from markets in China. In addition, the QuEChERS method can also be used for pretreatment of environmental samples. In 2019, Siti *et al.* [9] determined pesticide residues in rice soil and water by the combined application of the QuEChERS method and UPLC-MS/MS. The recovery of the method was controlled in 74% – 11% in soil and 77% – 117% in water.

Application of QuEChERS method in detection of pesticide residues in meat

Chen *et al.* [10] applied QuEChERS combined with GC-MS/MS to detect 34 kinds of pesticide residues in poultry. During the experiment, the main purification object of meat samples extracted by acetonitrile was lipid. At present, there are two kinds of materials known to be mainly used for purifying lipid: C18 and EMR degreasing purification tube. The authors of the study adopted a QuEChERS purification tube with more stable recovery (that is, a C_{18}-contianing purification tube) after experimental comparison. Thirty four kinds of pesticide residues in poultry meat were detected by this method. The average recovery of adding standard pesticides was about 78.22% – 118.79%, and the relative standard deviations were about 0.27% – 9.23%. Shen *et al.* [11] used QuEChERS combined with the 96-well solid-phase extraction (SPE) plate method to extract vancomycin and norvancomycin from fish samples, and analyzed them by UPLC-MS/MS/MS. The recovery of the experiment was between 86.7% and 98.6%. The results showed that the method could meet daily monitoring requirements of vancomycin and norvancomycin, and could be successfully applied to polluted and randomly collected samples.

Conclusions

The QuEChERS method is a relatively new pretreatment technique, but it has developed rapidly with a series of advantages such as high recovery, wide analysis range, fast detection speed and little environmental pollution. After nearly 20 years of development, it has been relatively mature in the fields of vegetables and fruits, medicines, and pesticide residues in deeply-processed products and so on. The continuously improved QuEChERS method can be used with various analyzers and detect a large number of pesticides at the same time, which provides very important help for pesticide residue analysts to carry out experiments. During experiments, scholars and analysts found that the QuEChERS purifying agents used in experiments also have a certain adsorption effect on purification targets, which greatly affects the recovery of pesticides. Therefore, it will be the focus of future research and improvement of the QuEChERS method to develop purifying agents that have obvious purification effect on sample impurities but weakly adsorb or even do not adsorb the targets.

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of antibiotics in water samples around landfill sites.

Conclusions and Discussion

This study established an LC-MS/MS analysis method that could simultaneously detect the contents of 26 antibiotics in the water surrounding the landfill site. The samples were enriched by an HLB solid-phase extraction column and then determined by LC-MS. The limits of detection ranged from 0.15 to 3.00 ng/L, and the limits of quantitation were between 0.80 and 10.00 ng/L, and the recoveries ranged from 77.9% to 104.85%. Three antibiotics were detected in the actual samples. Among them, ofloxacin had the highest detection frequency, and was detected at 8 detection points, with a detection rate of 61.5%. The detection concentration of sulfadimidine was the highest, with a value of 0.99 μg/L.

The results indicated that the method has high sensitivity and good accuracy. This study provides a rapid, accurate and reliable analysis method for the determination of antibiotics in the water around landfill sites, which has strong practical value.

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