# Analysis of 8 pyrethroid pesticides in soil and sediment by GC-MS

Pyrethroid pesticides are a broad-spectrum insecticide that can effectively control more than 140 species of pests, and have a good control effect on mites and underground pests. They are widely used in agriculture and daily life. Commonly used pyrethroid pesticides have estrogenic effects and reproductive endocrine toxicity, which can pollute the environment, water bodies and soil, and indirectly cause damage to the human immune system, cardiovascular system and nervous system, thus seriously endangering human health. The GB jointly issued by the National Health Commission, the Ministry of Agriculture and Rural Affairs and the State Administration for Market Regulation 2763-2019 "National Food Safety Standard Maximum Residue Limits of Pesticides in Food" clearly stipulates the scope of use and maximum usage of 11 pyrethroid pesticides and their isomers in vegetables and fruits . In 2019, the Ministry of Ecology and Environment first issued and implemented HJ 1023-2019 "Soil and Sediment Determination of 47 Pesticides including Organophosphorus and Pyrethroids Gas Chromatography-Mass Spectrometry" to standardize the detection methods of such pesticide residues in soil and sediments.

In this paper , referring to the HJ 1023-2019 standard , Analytical 3068 GC - MS was used to analyze 8 pyrethroid pesticides . The test results showed that the fitting coefficients $R^2$ of the 8 compounds were all greater than 0.9919, which met the requirement of the linear correlation coefficient $R^2 > 0.990$ of the calibration curve specified in HJ 1023-2019 ; the precision of all substances was between 0.48-2.42 %, with high stability; the detection limits of the 8 pyrethroids were between 0.10 - 0.17 The method verified by this instrument is stable and reliable, meets the analytical requirements of the standard , and can provide strong support for protecting people's health.

Gas chromatography-mass spectrometry (Analytical 3068 GC -MS , Analytical Technology Ltd.) .

8 kinds of pyrethroid mixed standard stock solution (1000 μg/mL), methanol (chromatographic grade), high-purity helium (purity ≥99.999%).

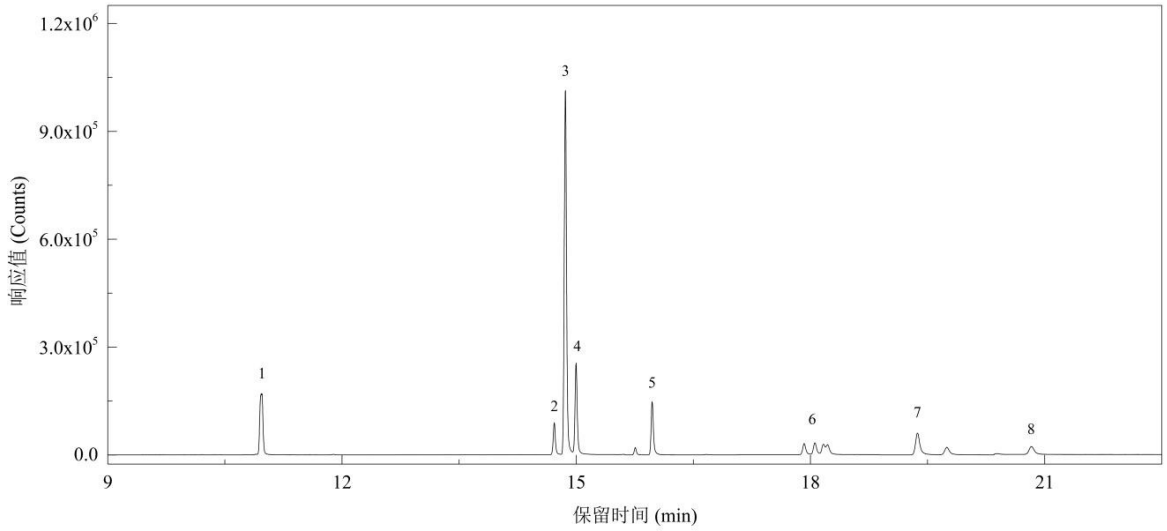
Using methanol as solvent, 8 pyrethroid standard stock solutions with a concentration of 1000 μg/mL were diluted to an intermediate solution with a concentration of 100 μg/mL . The intermediate solution was prepared into a series of standard samples with concentrations of 8.0 μg/mL , 4.0 μg/mL , 2.0 μg/mL , 1.0 μg/mL , 0.5 μg/mL and 0.25 μg/mL , of which the 0.25 μg/mL sample was used to test the instrument detection limit.

parameters of Analytical 3068 GC - MS gas chromatography-mass spectrometry are shown in Table 1 .

| | |
|---|---|
| Inlet temperature | 250 ℃ |

| | |
|---|---|
| Injection volume | 1 μL |
| Injection mode | Pulsed splitless injection /pulse pressure (time): 180 kPa (0.25 min) |
| Chromatographic columns | DB-5 MS, 30 m × 250 μm × 0.250 μm |
| Flow rate | 1. 0 mL/min , constant flow |
| Heating program | Initial temperature 100℃ , maintain for 1 min;<br>Increase the temperature to 230℃ at 15℃/min and hold for 2 min;<br>Increase the temperature to 280℃ at 10℃/min and maintain for 10 min<br>; |
| Transfer line temperature | 240℃ |
| Ion source temperature | 270℃ |
| Mass spectrometry scanning mode | EI, SIM (selected ions see Table 2) |

Figure 2 shows the separation effect of 8 pyrethroids on the DB-5MS column. All components achieved baseline separation and the separation effect of each substance was good.




Note: 1- propylene polyester ; 2 -tetramethrin ; 3- bifenthrin ; 4 -cypermethrin ; 5- cyhalothrin ; 6 -cypermethrin ; 7- cypermethrin ; 8- deltamethrin

## Standard curve

The external standard method was used for quantification, and the linear fitting coefficients $R^2$ of the eight pyrethroid components in the range of 0.25 μ g /mL-8.0 μ g / mL were all greater than 0.9919 , meeting the standard requirements. Detailed data are shown in Table 2 , and the standard fitting curves of some pyrethroids are shown in Figure 3 .

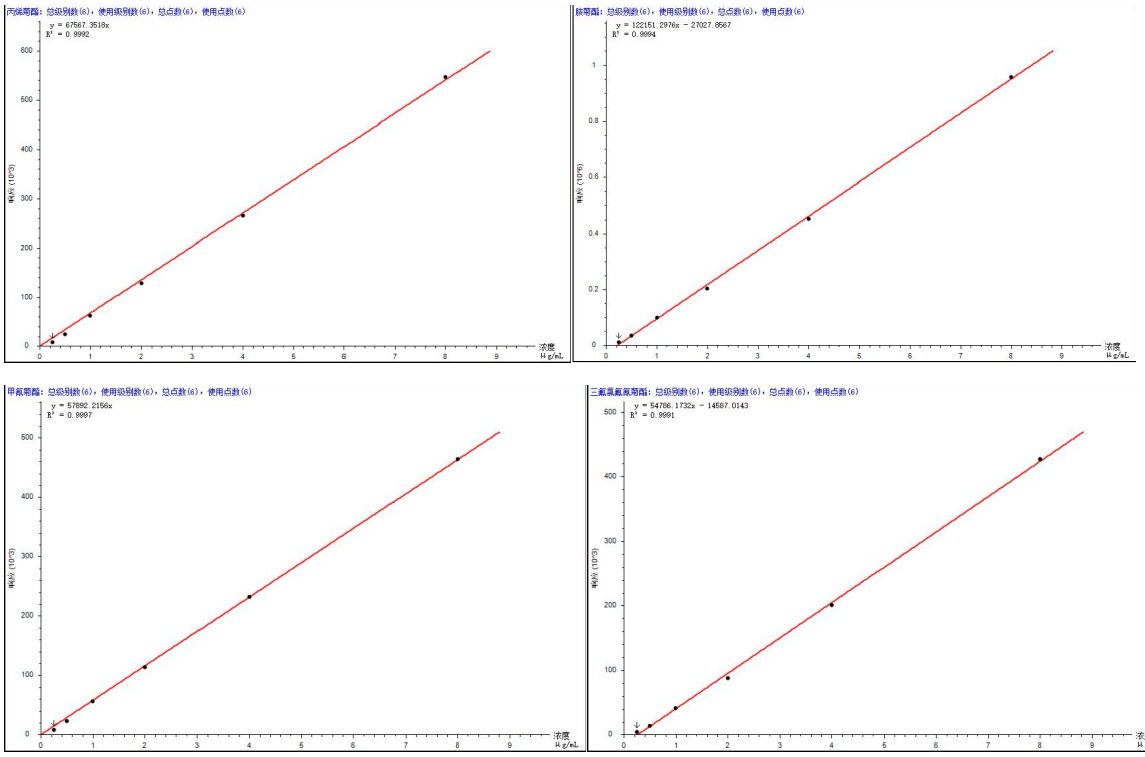
the analysis conditions in Table 1 , the chromatograms of 0.50μg /mL samples were collected seven times in succession, and the precision of the instrument method was calculated. The test results are shown in Table 2. The precision of the eight pyrethroids ranged from 0.48 to 2.42 % , with good stability .

The method detection limit (MDL) was calculated according to HJ 168-2020 "Technical Guidelines for the Development of Environmental Monitoring Analytical Method Standards". A sample of 250 μg/L was prepared , and the measurement was repeated 7 times under the instrument reference conditions, and the standard deviation S was calculated.

Formula: MDL = 3.143 × S

The results are shown in Table 2. The detection limits of the eight pyrethroids ranged from 0.10 to 0.17 .

mg/kg.



| Serial number | Components | CAS | Retention time (min) | Quantitative ion | Qualifier ions | $R^2$ | RSD (%) | MDL (mg/kg) |
|---|---|---|---|---|---|---|---|---|
| 1 | Allethrin | 584-79-2 | 10.98 | 123 | 79 | 0.9992 | 0.99 | 0.17 |
| 2 | Tetramethrin | 7696-12-0 | 14.74 | 164 | 123 | 0.9994 | 0.55 | 0.12 |
| 3 | Bifenthrin | 82657-04-3 | 14.86 | 181 | 165 | 0.9990 | 1.19 | 0.16 |
| 4 | Cypermethrin | 64257-84-7 | 15.02 | 97 | 55 | 0.9997 | 0.82 | 0.14 |
| 5 | Halcyhalothrin | 91465-08-6 | 15.99 | 181 | 197 | 0.9991 | 0.51 | 0.10 |
| 6 | Cypermethrin | 52315-07-8 | 17.95-18.24 | 163 | 181 | 0.9919 | 2.42 | 0.16 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | Cypermethrin | 52315-07-8 | 17.95-18.24 | 163 | 181 | 0.9919 | 2.42 | 0.16 |
| 7 | Fenvalerate | 51630-58-1 | 19.42-19.79 | 125 | 167 | 0.9940 | 0.51 | 0.11 |
| 8 | Deltamethrin | 52918-63-5 | 20.9 | 181 | 253 | 0.9925 | 0.48 | 0.10 |

An analytical method for analyzing eight types of pyrethroids was established using Analytical 3068 GCMS . The method verified by this instrument is stable and reliable, meeting the standard analysis requirements and providing technical support for protecting people's health.

The method analyzes the performance as follows

① $R^2$ of the eight pyrethroids were all greater than 0.9919;

② The precision is 0.48-2.42% ;

③ The detection limit is between 0.10 - 0.17 mg/kg .