SHIMADZU

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Rapid screening and quantitative analysis of pesticides in vegetables by UHPLC-Q-TOF-MS/MS

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1. Overview

In this paper, a rapid qualitative and quantitative method for the determination of 49 routine pesticides in vegetables by LCMS-9030 ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry was established.

2. Introduction

The method is simple and fast. After extraction by acetonitrile, samples are salted out, centrifuged, filtered, and then directly injected for analysis; the analysis speed is fast, the detection time is only 15 minutes; the sensitivity is high, the detection limit is 0.01 ng/mL - 0.75 ng/mL; the linear relationship is good, the correlation coefficient r is greater than 0.99; the precision is good, RSD is less than 5%; the quality is excellent, accuracy and first-class quality. The accuracy of spectral mass number is less than 1 ppm, the isotope distribution is true and accurate, and the matching degree of secondary spectral library is high. The method is simple, rapid, sensitive, accurate and stable for qualitative and quantitative screening, and can be used for rapid qualitative screening and quantitative detection of pesticide residues in vegetables.

3. Methods and Materials

Sample extraction:

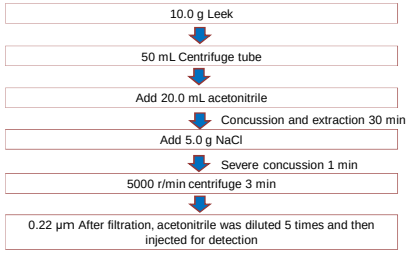

Figure 1 Sample pretreatment steps

LCMS-9030
Our core messages
Sensitivity and Speed
Routine high mass accuracy
High mass stability

Figure 2 LCMS-9030 Quadrupole Time of Flight Mass Spectrometry

Instrument conditions:

Table 1 Conditions of HPLC

column	:	Shim-pack GIST 2.1 mm I.D. ×100 mm 2 μm
Mobile phase	:	A: 1mM Ammonium acetate in water; B: Methanol
speed	:	0.4 mL/min
Column temperature	:	45℃
Injection volume	:	1 μL

Table 2 Time program

Time(min)	Command	Value
1.00	Pump B Conc.	30
10.00	Pump B Conc.	95
12.00	Pump B Conc.	95
12.01	Pump B Conc.	10
15.00	Stop	

Table 3 Conditions of MS

Ion source	: ESI+/-	**Heatblock Temperture**	: 500℃
Nebulizer Gas	: 3.0 L/min	**Drying Gas**	: 10.0 L/min
Heating Gas	: 10.0 L/min	**DL Heatblock Temperture**	: 150℃
Interface Temperture	: 500℃	**Loop time**	: 0.6 s
Scan Mode	: MS full scan m/z: 130-1000 MSMS(DDA) m/z: 50-950 CE: 30±20 V		

4. Result

Qualitative screening results:

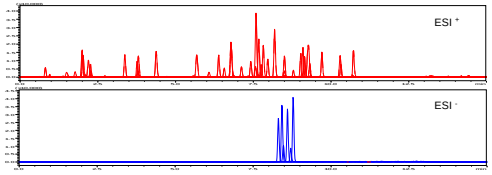

Figure 3 5 ng/mL EIC of 49 pesticides in Leek

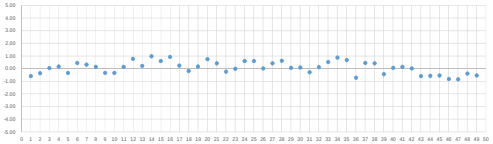

Figure 4 Relative error of 49 pesticides （ppm）

The pesticides screening list established by this method was used to extract the EIC of 49 pesticides from leek samples. The retention time of the EIC was confirmed to be the same as that of the mixed pesticides in the list.

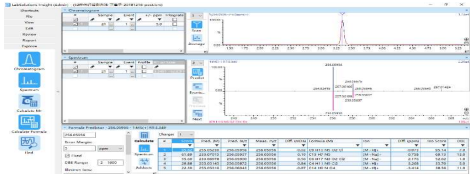

Figure 5 Evaluation results of imidacloprid isotope distribution

The results show that the matching degree between the measured and theoretical isotope distributions is 95.14%. The predicted first molecular formula is consistent with imidacloprid.

Figure 6 Matching Evaluation of Imidacloprid Secondary Mass Spectrometry Library

The MS^2 secondary mass spectrometry Library of 49 pesticides was established. After searching for the secondary mass spectrometry library, the similarity between the MS^2 mass spectra of imidacloprid detected in the leek standard-added samples and the mass spectra of different CE energies in the library could reach more than 80%.

The chromatographic peaks extracted from routine pesticide screening lists were consistent with the corresponding pesticide varieties by synthesizing the evaluation results of retention time, accuracy of mass, isotope distribution and matching of secondary mass spectrometry libraries.

Quantitative test results:

Sensitivity results:

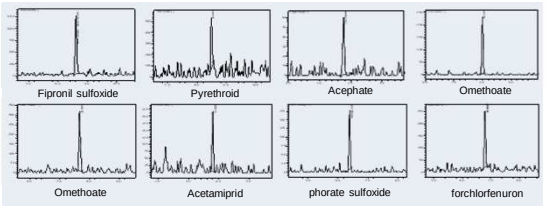

Figure 7 EIC of 0.1 ng/mL Partial Pesticide Mixed Standard

Investigation of Linear:

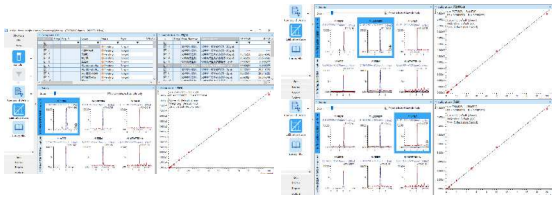

Figure 8 Part of the standard curve of pesticides

Precision Investigation:

Figure 9 Part of precision results of pesticides

5. Conclusions

In this paper, a rapid qualitative and quantitative method for the determination of 49 routine pesticides in vegetables by LCMS-9030 ultra-high performance liquid chromatography quadrupole time-of-flight mass spectrometry was established. Through simple and fast sample pretreatment and rapid, accurate qualitative and quantitative detection method, the pesticides of the routine monitoring in leek standard-added samples analyzed, and the method was evaluated. The evaluation results show that the method has fast analysis speed, detection time is only 15 minutes; high sensitivity, detection limit is 0.01 ng/mL - 0.75 ng/mL; good linear relationship, correlation coefficient r is greater than 0.99; good precision, RSD are less than 5%. It has excellent mass accuracy, mass accuracy of MS^1 is less than 1 ppm, isotope distribution is true and accurate, and matching degree of MS^2 spectrum library is high. After comprehensive investigation, the method is simple, rapid, sensitive, accurate and stable, and can be used for rapid qualitative screening and quantitative detection of pesticide residues in vegetables.