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Determination of Organic tin pesticides in fruits and vegetables by gas chromatography coupled to tandem mass spectrometry

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Xiaohua Liu[1], Ying Ye[2], Hui Hu[1], Wenyi Kang[1], Caihong Xiang[1], Jingting Yao[1], Taohong Huang[1], Shin-ichi Kawano[1], Yuki Hashi[1]
[1]Shimadzu Global COE (Center of Excellence) for Application&Technical Development,
[2]Shimadzu (China) Co., Ltd Guangzhou 510010, China

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Introduction

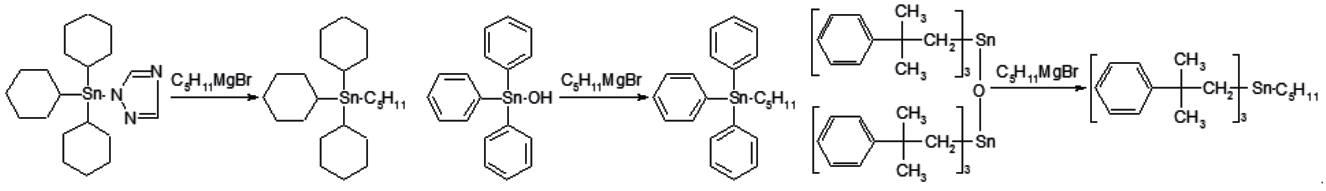
Organic tin pesticides are often used to sterilize and kill of mites in fruits and vegetables. This kind of pesticides is dangerous substance with high toxicity, and some of them can cause cancers. The latest implementation of the food safety standards of china sets the maximum residue limit of azacyclotin and fenbutatin oxide in apple, organges, etc, which range from 0.1 mg/kg to 2.0 mg/kg. At present, the methods of detecting organic tin pesticides in China and abroad are mainly by GC and GC/MS. Because of the complexity of vegetable and fruit matrix, the method of GC and GC/MS is very complicated. A method for the simultaneous detection of azacyclotin, triphenylhydroxytin and fenbutatin oxide residues in fruits and vegetables was developed by pentylmagnesium bromide derivatization and GC-MS/MS. This method shows strong anti-interference capability, accuracy and high sensitivity to detect organic tin pesticides in fruits and vegetables.

Methods and Materials

Sample Preparation

The sample was firstly extracted by acetone and hexane, followed derivatization with pentylmagnesium bromide. Then after purification using Envi-Carb and florisil SPE columns, the sample extracts were finally analyzed by GC-MS/MS instrument.

Sample Preparation



Azocyclin | Triphenyltin hydroxide | Fenbutatin oxide

GC/MS/MS analysis

GC Conditions:	
Analytical column	: Rtx-5 ms (30 m×0.25 mm×0.25 μm) (Restek,Japan)
Inlet temp	: 300 °C
Temperature program	: 50 °C (1 min)_20 °C/min_300 °C (7 min)
Control mode	: constant Linear Velocity (35.7 cm/sec)
Splitless injection	
Injection Volume	: 1 μL
MS Conditions:	
Ionization mode	: EI
Ion source temperature	: 250 °C
IF temperature	: 300 °C
Acquisition mode	: MRM (parameter showed in Tab.2)

Results and Discussion

Analytes' specific MS/MS parameters (Quantitative ion pair, Quanlitative ion pair and collision energy) were ato-optimized using Smart MRM/SIM software function provided in GCMS-Solution. The compound information for organic tin pesticides and MS/MS parameters for organic tin pesticide derivatives are shown in Table 1 and Table 2.

Table 1 The compound information of 3 organic tin pesticides

Compound name	CAS Number
Azocycltin	41083-11-8
Triphenyltin,hydroxide	76-87-9
Fenbutatin oxide	13356-08-6

Table 2 The MRM parameter of organic tin pesticide derivatives

No.	Compound name	Retention Time (min)	Quantitative ion pair (m/z)	CE (v)	Quanlitative ion pair (m/z)	CE (v)	Quanlitative ion pair (m/z)	CE (v)
1	Azocycltin derivative	13.472	205.00>81.10	6	287.00>205.10	18	287.00>81.10	18.00
2	Triphenyltin,hydroxide derivative	13.519	351.00>197.00	27	351.00>120.00	27	349.00>194.90	27.00
3	Fenbutatin oxide derivative	18.106	457.00>275.00	24	455.00>273.00	30	457.00>197.00	30.00

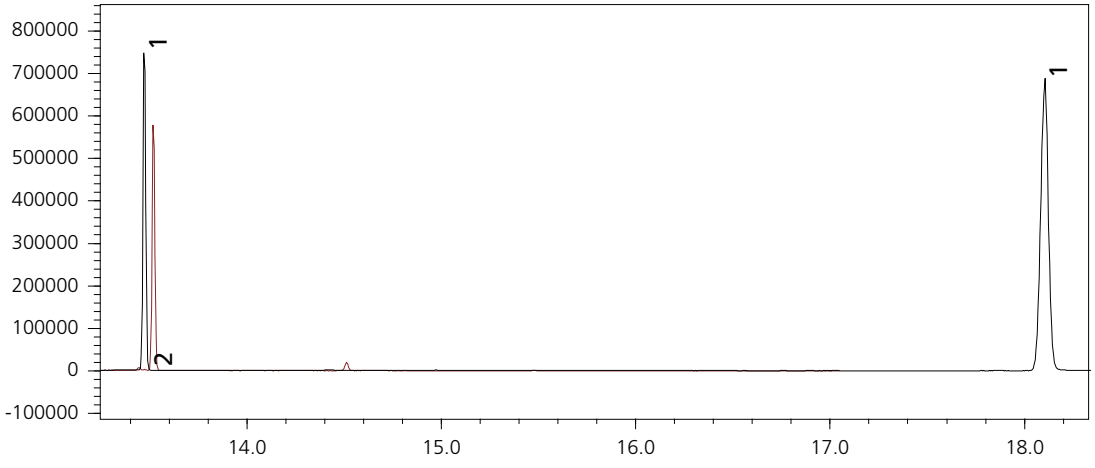


Figure 1 MRM chromatogram of organic tin pesticide derivatives (1.0 mg/L each)

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Under the optimal pretreatment conditions, a series of working standard solutions were prepared and derivatived using pentylmagnesium bromid, the derivatives were extracted by hexane, concentrated and constant volume, the concentrations were 0.005, 0.01, 0.05, 0.1 and 0.5 mg/L. The derivative solution was analyzed under the selected chromatographic and mass spectrometric conditions, the calibration curve and the relative coefficients (r) were showed in Fig.2. The monitoring ions of derivative components are shown in Tab.2.

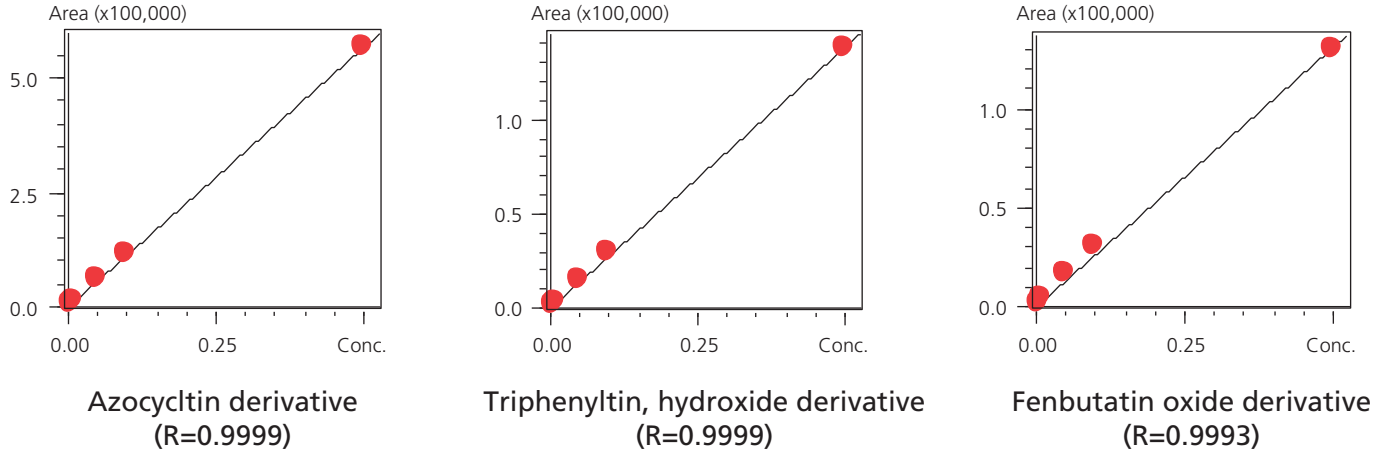

Fig.2. The calibration curve of organic tin pesticide derivatives

In this paper, we also study the reproducibility of the instrument, the recovery of the method and the real detection limit of organic tin pesticide derivatives. The mixture organic tin pesticide derivative solution (c=0.01 mg/L) was injected 5 times, the relative standard deviation (RSDs) from 1.8% to 3.7%, the result is shown in Tab.3. Two blank matrix samples (cabbage, mustard, pear and apple) were prepared respectively, the recovery experiments were conducted by spiking one blank matrix sample, the spiking concentration was 0.01 mg/kg, the mean recoveries were from 74.1% to 124.5%, the result is shown in Tab.4. The mixture organic tin pesticides solution was diluted and derivatived using pentylmagnesium bromid. The real detection limit of organic tin pesticide derivatives were 1 μg/L. The mass chromatogram of the derivatives were showed in Fig.3. This method was used to detect organic tin pesticides in cabbage sample, the MRM chromatogram of sample was showed in Fig.3 and the result was showed in Tab 5. The result was accurate and reliable.

Table 3 The repeatability result of organic tin pesticide derivatives (n=5)

Compound name	Area 1	Area 2	Area 3	Area 4	Area 5	Mean Area	RSD(%)
Azocycltin derivative	5255	5397	5433	5535	5017	5327	3.7
Triphenyltin,hydroxide derivative	1306	1307	1307	1291	1226	1287	2.7
Fenbutatin oxide derivative	1576	1547	1556	1619	1569	1573	1.8

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Table 4 The recovery of different samples (%)

Compound name	cabbage	mustard	pear	apple
Azocycltin derivative	100.9	113.9	84.6	91
Triphenyltin,hydroxide derivative	88.3	85.8	74.1	81.6
Fenbutatin oxide derivative	124.5	86.4	88.4	95.2

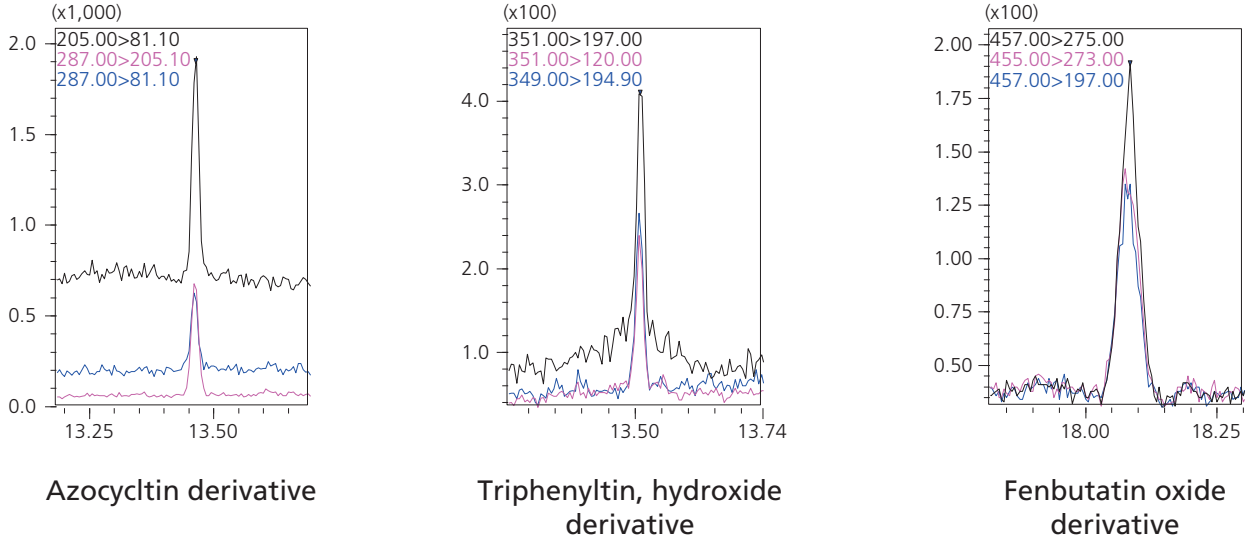

Fig.3. The mass chromatogram of the organic tin pesticide derivatives (1 µg/L each)

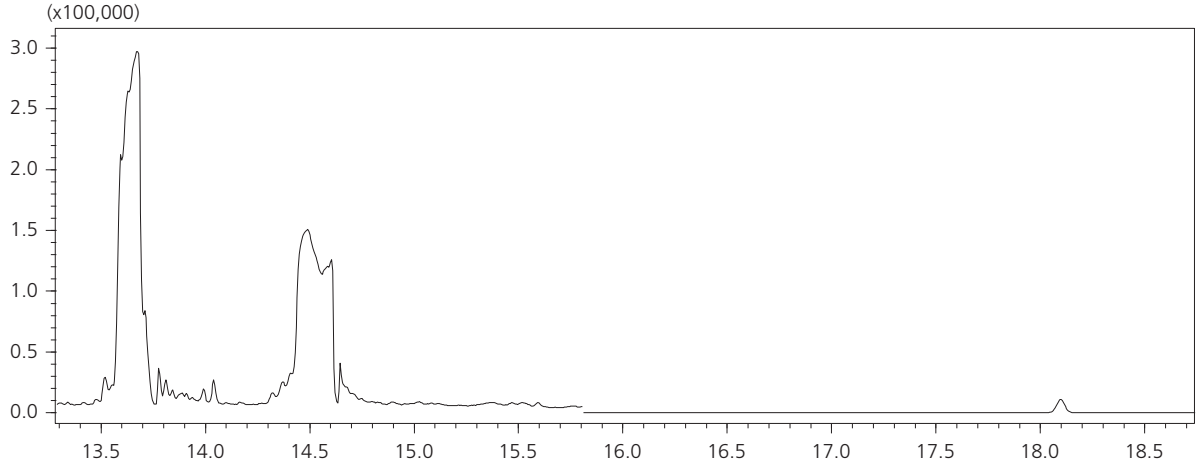

Fig.4. MRM chromatogram of sample

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Table 5 The result of sample

No.	Compound name	Retention Time(min)	content (mg/kg)
1	Azocycltin	13.472	-
2	Triphenyltin,hydroxide	13.519	-
3	Fenbutatin oxide	18.106	24491

Conclusions

The method of detection 3 organic tin pesticides in vegetables and fruits was established using GCMS-TQ8040. The sample was extracted with acetone and hexane, derived by pentylmagnesium bromide, then cleaned up with activated carbon and florisil solid phase extraction column, and detected by the GC-MS/MS system. It showed good linearity within the range of 0.005 mg/L to 0.5 mg/L. The recoveries of the method ranged from 74.1% to 124.5%. The mixture organic tin pesticide derivative solution was injected 5 times, the relative standard deviation were less than 5.0%, with good precision. The method is simple, can provide effectively support to the detection of organic tin pesticides in vegetables and fruits.

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