AccuTOF-GCv Series

Quantitative Analysis of Pyrazole Pesticides in Tea Leaf by Using FastGC-HRTOFMS

Introduction

The FastGC method is a very useful technique for doing rapid GC analyses that result in extremely narrow chromatographic peaks over a shorter time period than traditional GC analyses. Additionally, time-of-flight mass spectrometers (TOFMS) are capable of very fast data acquisition in comparison with other types of mass spectrometers so they are well suited as the detector for the FastGC technique. Furthermore, when the TOFMS is capable of high resolution measurements, the resulting mass spectra contain accurate mass information that can be used to calculate the elemental compositions for each observed *m/z*.

In this application note, we describe the quanitative analysis of pyrazole pesticides (Fipronil, Ethiprole, Pyraflufen ethyl and Tebfenpyrad) on tea leaves by FastGC/HRTOFMS. Additionally, we confirm that a rapid analysis with high sensitivity is easy to perform and very useful for fast screening.

Method

The instrument measurement conditions are shown in Table 1.

Table 1. GC/MS measurement conditions.

Instrument	JMS-T100GCV (JEOL)
Quantitative software	Escrime (JEOL)
Injection mode	Splitless
Injection temp.	250℃
Oven temp. program	40℃(1min) → 50℃/min → 300℃(3.8min)
Injection volume	1μL
Column	DB-5, 10m x 0.18mm, 0.18μm
Carrier gas	He, 0.7mL/min, Const. flow
Ionization mode	EI+, 70eV, 300μA
Ion source temp.	250℃
m/z range	m/z 35 - 500
Spectrum recording time	0.1sec

The tea leaf sample (5g) was prepared using the multiresidue method for agricultural chemicals by GC/MS published by Ministry of Health, Labour and Welfare, Japan. The pyrazole pesticides were added to make 0.01, 0.05 and 0.1ppm solution in the prepared solution from tea leaf. These concentrations in solution are equivalent to 4, 20 and 40ppb in tea leaf. Each sample was analyzed 3 times to check the reproducibility of the results.

Results and discussion

Fig.1 shows an expanded mass spectrum of a 0.01ppm sample solution (4ppb in tea leaf) of Fipronil. This spectrum shows the *m/z* 254.97 ion produced by Fipronil and the ion of *m/z* 255.21 produced by a contaminant. When low-resolution MS such as QMS is used, these ions cannot be separated from each other. However, as Fig.1 shows, the HR-TOFMS can easily separate these ions from each other. Therefore, it is possible to create high-resolution mass chromatogram with narrow *m/z* window (±0.05 Da) in order to eliminate the influence of chemical background. Fig.2 shows high-resolution mass chromatograms for each pesticide in the 0.01ppm sample solution.

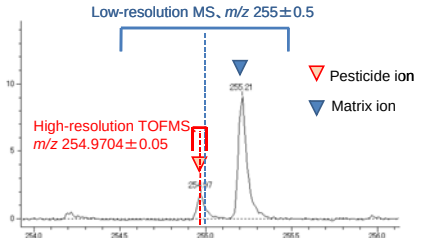

Fig. 1 Mass spectrum of Fiprinol

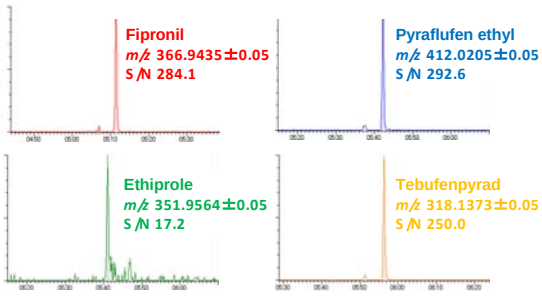

Fig.2 High-resolution Mass chromatograms of 0.01ppm

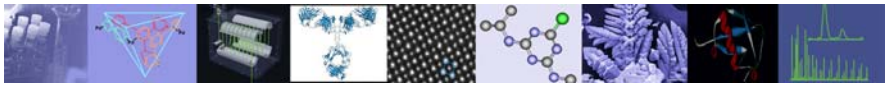

Fig.3 shows the calibration curves and Table 2 shows the reproducibility (n=3) for each pesticide. The Japanese default maximum regulated residues level (MRLs) for Fipronil is 2ppb and for Pyraflufen ethyl is 10ppb. The averaged S/N for each chromatographic peak in the 0.01 ppm sample solution (4ppb in tea leaf) is shown in Fig.2. For both Fipronil and Pyraflufen ethyl, the S/N is almost 300 and is more than sufficient for analyzing concentrations at or below the MRL value. Furthermore, the correlation coefficient for each pesticide is better than 0.997 which shows very good linearity across the concentrations that were tested. The reproducibility (n=3) is shown in Table2. The coefficient variation C.V. (%) was approximately 10% for each pesticide at each concentration which shows very good reproducibility.

Conclusions

These results shows that the JMS-T100GCV used with FastGC can easily obtain good quantitative result with high spectrum sensitivity, high mass accuracy and high resolution even if sample includes chemical contaminants.

Reference

M. Ubukata et al., Abstract of the 97th conference of the Japanese Society for Food Hygiene and Safety, page 20 (2009).

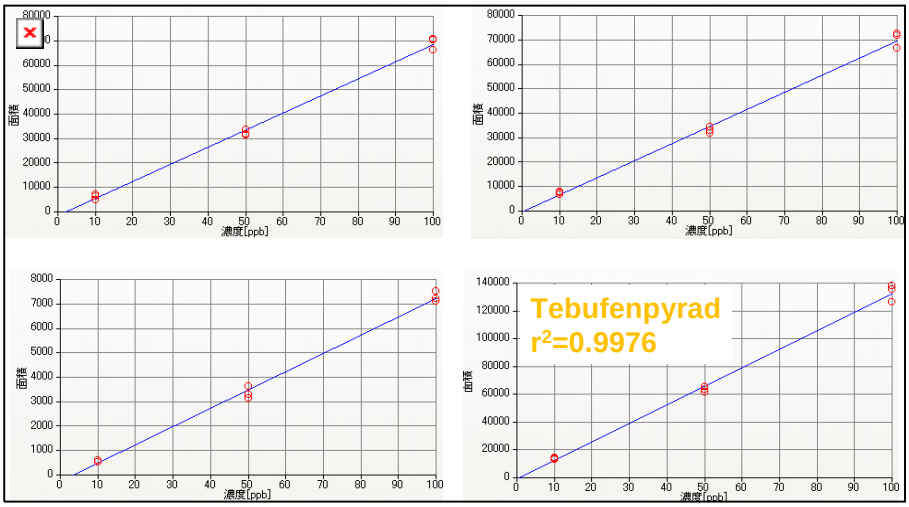

Fig.3 Calibration curves

Table 2. Results of quantitative analysis.

ppm	No.	Fipronil	Ethiprole	Pyraflufen ethyl	Tebufenpyrad
0.01	1	9.39	10.51	10.47	10.58
	2	11.37	10.51	11.49	11.26
	3	11.81	11.85	11.65	10.8
	Ave.	10.86	10.96	11.20	10.88
	C.V.(%)	11.87	7.06	5.71	3.19
0.05	1	49.73	47.36	49.57	49.84
	2	46.78	45.64	46.1	47.06
	3	47.37	51.84	49.57	48.35
	Ave.	47.96	48.28	48.41	48.42
	C.V.(%)	3.25	6.63	4.14	2.87
0.1	1	101.06	99.98	104.01	102.29
	2	95.44	98.32	95.63	95.43
	3	101.66	104	103.25	104.39
	Ave.	99.39	100.77	100.96	100.70
	C.V.(%)	3.45	2.90	4.59	4.65