JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
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No.148

JMS-T100GCV Application Data

Quantitative analysis of pyrazole pesticides in tea leaf using FastGC-HRTOFMS

[Introduction]

FastGC method is a very useful technique for rapid GC analysis. On the other hand, GC-TOFMS has the capability to acquire data very fast in comparison with other types of mass spectrometer. Therefore, TOFMS is most suitable mass spectrometer to combine with FastGC method. In combination with the high resolution capability (HR-TOFMS) we can obtain very accurate spectra with exact m/z determination.

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

[Sample and method]

Measurement conditions are shown in Table 1. Tea leaf (5g) was prepared using the multiresidue method for agricultural chemicals by GC/MS published by Ministry of Health, Labour and Welfare, Japan. Pyrozole 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.

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

[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 can not be separated. However, as Fig.1 shows, HR-TOFMS can separate each ion easily.

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.

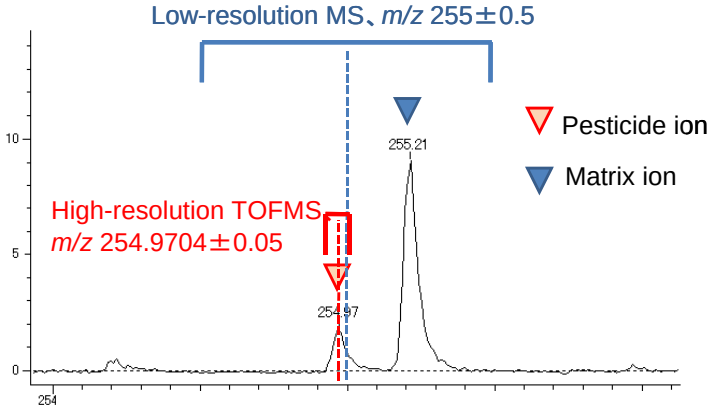

Fig.1 Mass spectrum of Fipronil.

Fig.2 shows high-resolution the mass chromatograms for each pesticide in a 0.01ppm sample solution.

Fig.3 shows the calibration curves and Table 2 shows the reproducibility (n=3) for each pesticide. 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 a 0.01 ppm sample solution (4ppb in tea leaf) is shown in Fig.2. For both Fipronil and Pyraflufen ethyl, this is almost 300. This S/N is enough to analyze them even if these concentrations are around the MRL value. Furthermore, the correlation coefficient for each pesticide is more than 0.997 and it shows very good linearity. The reproducibility (n=3) is shown in Table2. The variation coefficient C.V. (%), of about 10% for each pesticide at each concentration, demonstrates good reproducibility.

This result shows that the JMS-T100GCV can easily obtain good quantitative result with high spectrum sensitivity, high mass accuracy and high resolution even if sample including chemical contaminants.

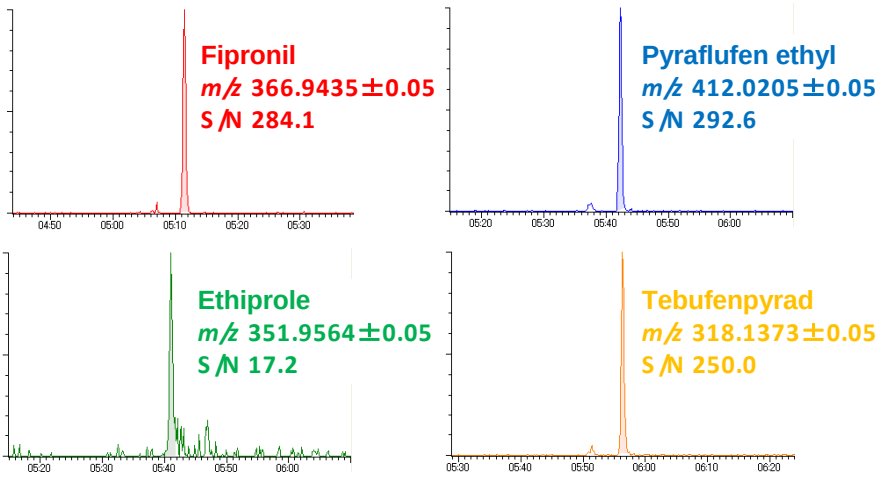

Fig.2 High-resolution Mass chromatograms of 0.01ppm

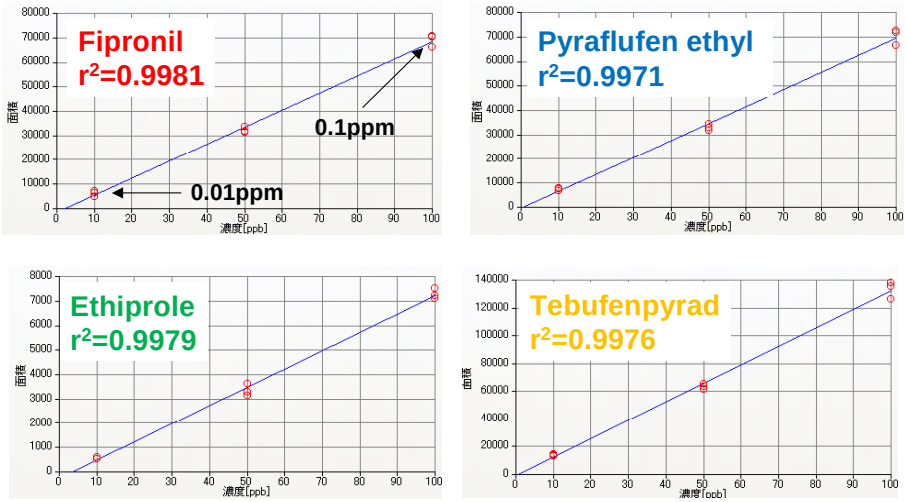

Fig.3 Calibration curves

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

[Reference]

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