JEOL MS Data Sheet

MS Tips

Mass Spectrometry Application Group
Mass Spectrometry Business Unit
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JMS-T100GCV Application Data

Qualitative analysis of pyrazole pesticides in tea leaf by using FastGC-HRTOFMS

[Introduction]

FastGC method is a very useful technique for rapid GC analysis. On the other hand, GC-TOFMS has the capability of very fast data acquisition in comparison with other types of mass spectrometers. Therefore, TOFMS is most suitable to combine with the FastGC technique. 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 TIC chromatogram and mass chromatograms of each pesticide. Pyrazole pesticides are detected within 6 minutes by using the FastGC method. Expanded mass chromatogram of Fipronil is shown in the right side of Fig.1. The peak width becomes very narrow in the FastGC methods.

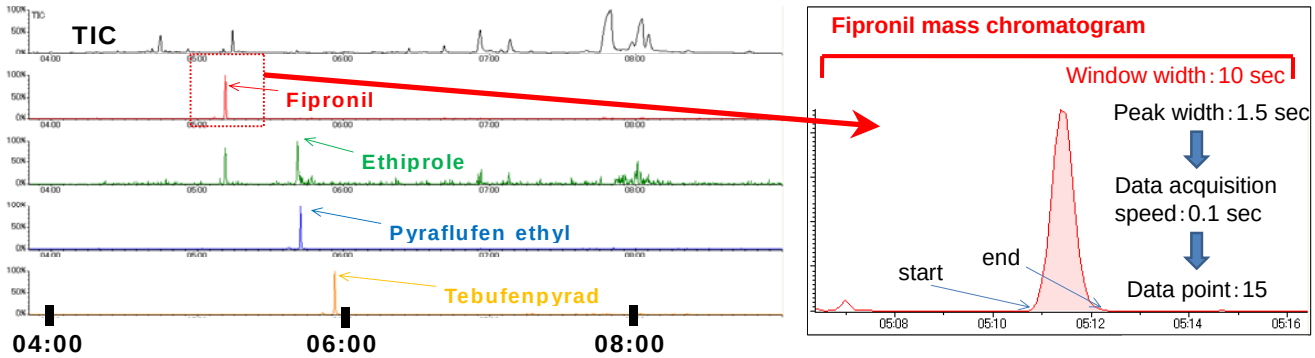

Fig.1 TIC chromatograms and Mass chromatograms

Now, the maximum recording interval on JMS-T100GCV is 0.04 seconds/spectrum (25Hz). When 0.1 seconds/spectrum (10Hz) of recording interval is used in this analysis, about 15 data points are acquired per chromatographic peak and this is enough to get good peak profile.

Mass spectrum of Fipronil is shown in Fig.2. Chemical backgrounds from tea leafs are observed prominently even at very low concentrated solution. However, characteristic ions of Fipronil such as *m/z* 350.95, 366.94 and 419.94 are observe and Fipronil is identified as first choice using NIST database search even in 0.01 ppm sample solution (4 ppb in tea leaf). In addition, mass accuracy for *m/z* 350.95, 366.94 and 419.94 is within 2.0x10^{-3}u. Table 2 shows the mass accuracy for characteristic ions of each pyrazole pesticide at different concentrations.

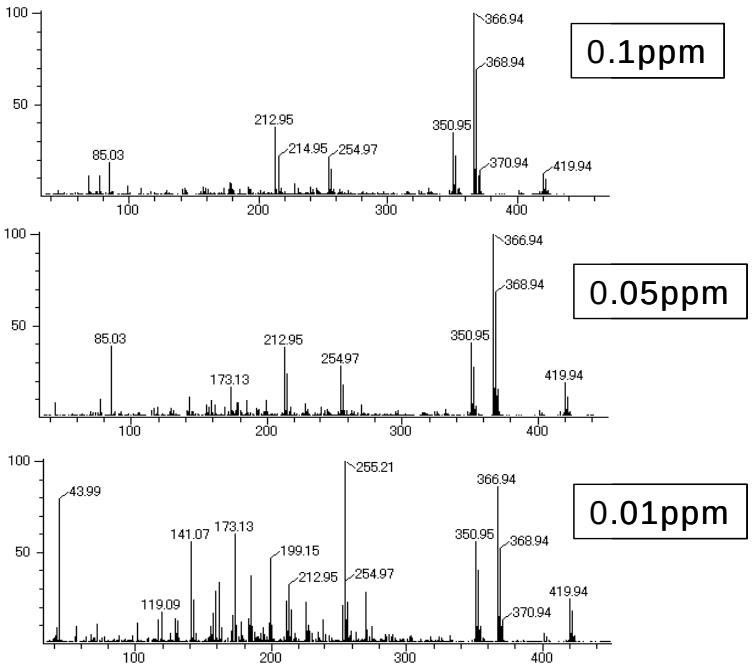

Fig.2 Mass spectra of Fipronil.

JMS-T100GCV can easily obtain good data with high spectrum sensitivity and high mass accuracy even if sample includes chemical contaminants. Identification using accurate mass is very useful in addition to the database search.

Table 2 Results of exact mass measurements.

Fipronil

ion	$C_{11}H_4Cl_2F_3N_4S$	$C_{11}H_4Cl_2F_3N_4OS$	$C_{12}H_4Cl_2F_6N_4S$
Calc. exact mass	350.9486	366.9435	419.9438

ppm	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)
0.1	350.9473	−1.3	366.9417	−1.8	419.9435	−0.3
0.05	350.9472	−1.4	366.9423	−1.2	419.9425	−1.3
0.01	350.9474	−1.2	366.9431	−0.4	419.9449	1.1

Pyraflufen ethyl

ion	$C_{12}H_8Cl_2F_3N_2O_2$	$C_{13}H_9ClF_3N_2O_4$	$C_{15}H_{13}Cl_2F_3N_2O_4$
Calc. exact mass	338.9915	349.0203	412.0205

ppm	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)
0.1	338.9917	0.2	349.0194	−0.9	412.0212	0.7
0.05	338.9911	−0.4	349.0184	−1.9	412.0207	0.2
0.01	338.9914	−0.1	349.0191	−1.2	412.0201	−0.4

Ethiprole

ion	$C_8H_4Cl_2F_3N_2$	$C_{11}H_5Cl_2F_3N_4S$	$C_{13}H_9Cl_2F_3N_4S$
Calc. exact mass	254.9704	351.9564	379.9877

ppm	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)
0.1	254.9722	1.8	351.9577	1.3	379.9894	1.7
0.05	254.9721	1.7	351.9547	−1.8	379.9885	0.8
0.01	254.9767	6.4	351.9563	−0.1	379.9897	2.0

Tebufenpyrad

ion	$C_7H_8ClN_2O$	$C_{17}H_{21}ClN_3O$	$C_{18}H_{24}ClN_3O$
Calc. exact mass	171.0325	318.1373	333.1608

ppm	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)	Meas. exact mass	Error (10^{-3}u)
0.1	171.0343	1.8	318.1379	0.6	333.1617	0.9
0.05	171.0335	1.0	318.1383	1.0	333.1614	1.7
0.01	171.0333	0.8	318.1388	1.5	333.1616	0.8

[Reference]

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