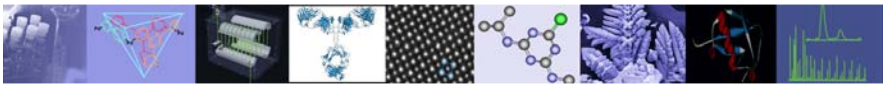

Applications Note

AccuTOF-GCv Series

Qualitative 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 qualitative 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. Pyrozole pesticides were added to make 0.01, 0.05 and 0.1ppm solutions in the prepared solution from tea leaf. These concentrations are equivalent to 4, 20 and 40ppb on the tea leaf material. Each sample was then analyzed 3 times to check the reproducibility of the results.

Results and Discussion

Fig.1 shows the TIC chromatogram and mass chromatograms of each pesticide. Pyrazole pesticides are detected within 6 minutes by using the FastGC method. An expanded mass chromatogram of Fipronil is also shown in Fig.1. The peak width becomes very narrow in the FastGC methods.

The maximum recording interval on JMS-T100GCV is 0.04 seconds/spectrum (25Hz). However, when a 0.1 seconds/spectrum (10Hz) recording interval is used in this analysis, approximately 15 data points are acquired per chromatographic peak which is sufficient for achieving good chromatographic and mass spectral peak measurements.

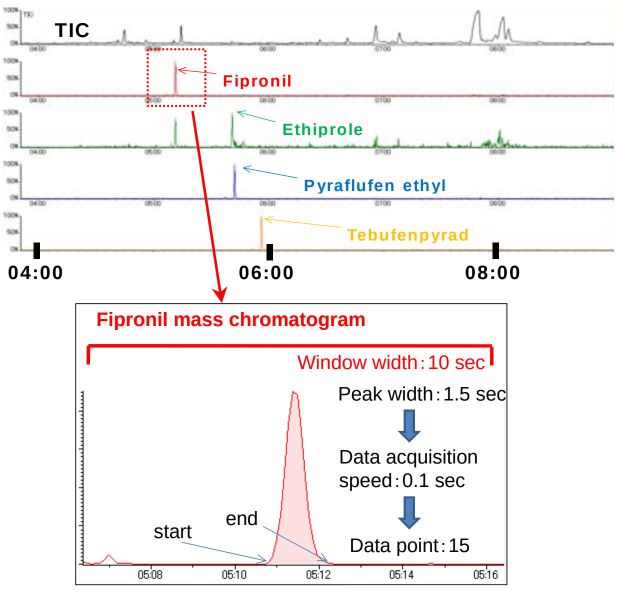

Fig.1 TIC chromatograms and mass chromatograms

MS Tips #147

The mass spectrum of Fipronil is shown in Fig.2. Chemical background peaks from the tea leafs were prominently observed even at very low solution concentrations. However, characteristic ions of Fipronil such as *m/z* 350.95, 366.94 and 419.94 were observed, and Fipronil was identified as the best match from the NIST database search even in the 0.01 ppm sample solution (4 ppb in tea leaf). Furthermore, the mass accuracy for *m/z* 350.95, 366.94 and 419.94 was within 2mmu of there expected exact masses. Table 2 shows the mass accuracy for the characteristic ions for each pyrazole pesticide at different concentrations; all of them showed errors of ≤ 2mmu.

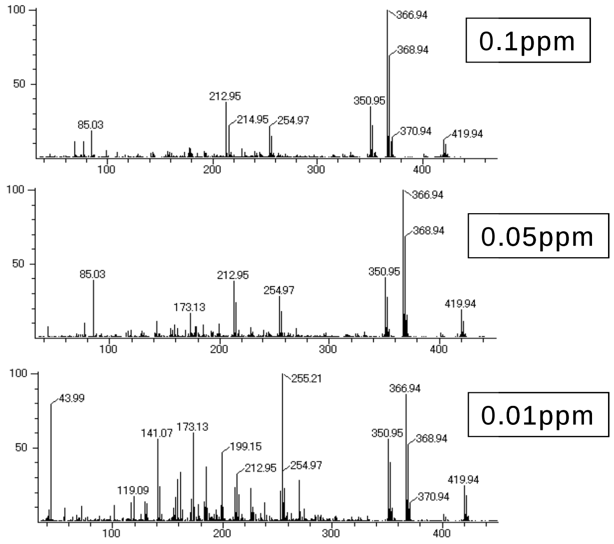

Fig.2 Mass spectra of Fipronil.

Conclusions

The AccuTOF-GCv used with FastGC can easily measure good quality data with high sensitivity and high mass accuracy even when the sample contains chemical contaminants. Furthermore, the accurate mass results provide additional confirmation to the mass spectral database searches that are typically done for compound identification.

Reference

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

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