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Use of Methylamine PICI for Qualitative Analysis by GC/Q-TOF

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Introduction

The demand for comprehensive qualitative analysis by GC/MS is increasing in all fields. In general, EI mass spectrum libraries are used for qualitative analyses by GC/MS, but there are many compounds that do not provide a hit in commercially available libraries.

GC/Q-TOF, with high resolution and MS/MS capabilities, has excellent qualitative abilities for such unknown compounds by utilizing positive ion chemical ionization (PICI). An ideal PICI trait is that protonated molecule and/or cationized molecules can appear and be identified in many compounds. The outline of a typical qualitative workflow by GC/Q-TOF is shown in Figure 1.

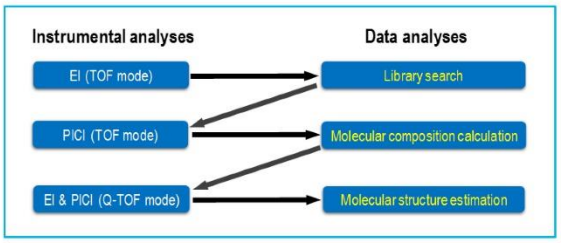

Figure 1. GC/Q-TOF qualitative workflow.

Methane, isobutane and ammonia are generally used as reagent gas, but protonated molecule and cationized molecules can not necessarily be obtained. Although it is known that amines have the possibility of being a very soft PICI reagent gas at the research level[1], it is not very practical. We confirmed that 2% methylamine (MA) in methane is easy to obtain cationized molecules even in compounds that are difficult with other reagent gases[2].

In this study, 2% MA in methane as well as pure methane were applied to commercially available insecticide, and many qualitative compound aspects could be obtained.

Experimental

Spray-type liquid household insecticide (0.5 mL) was collected in a sample vial. Acetone was added to make 1mL to use as the analytical sample.

Analysis was performed by Agilent 7200B GC/Q-TOF combined with Agilent 7890B GC. The analytical conditions are described in Table1.

Experimental

Gases in the cylinder were purchased and used as reagent gas (Takachiho Chemical Industrial, Tokyo, Japan). The flow rate of 2% MA in methane is the value optimized in the preliminary experiment, the flow rate of pure methane is the recommended value of Agilent.

Table 1. GC/Q-TOF operational conditions.

Instrument	
GC	Agilent 7890B
Autosampler	Agilent PAL2
MS	Agilent 7200B GC/Q-TOF
GC Conditions	
Column	DB-5ms, 30 meter, 0.25 mm ID, 0.25 µm film
Injection volume	1 µL
Split mode and ratio	Split 100:1-10:1 (Demands on measurement mode)
Split/Splitless inlet temperature	250 °C
Oven temperature program	100 °C
	15 °C/min to 325 °C, 2.0 min hold
Carrier gas	Helium at 1.2mL/min constant flow
Transfer line temperature	300 °C
MS Conditions	
Ionization mode	EI and PICI
PICI reagent gas	Methane at 20% flow
	2% MA in Methane at 10% flow
Source temperature	250°C for EI
	180°C for PICI
Quadrupole temperature	150°C

Results and Discussion

Peak Identification by library search

A total of 50 or more components were obtained by deconvolution. In this presentation, we will cover nine peaks with the largest area as shown in Figure 2. Seven of them were identified by library search of EI mass spectra using NIST database. They are listed in Table2. However, the other two (No.2 and No.8) did not hit.

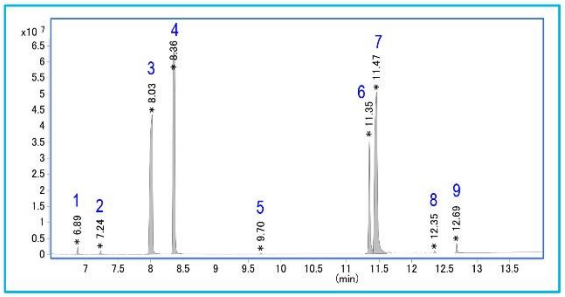

Figure 2. Total ion current chromatogram obtained by EI.

Results and Discussion

Table 2. Compounds identified by library search.

No.	R.T.	Compound	CAS	Molecular fomula	M.W.	DBE
1	6.89	Isopropyl laurate	10233-13-3	C15H30O2	242.2246	1
2	7.23					
3	7.98	Metoxadiazone	60589-06-2	C10H10N2O4	222.0641	7
4	8.34	Isopropyl myristate	110-27-0	C17H34O2	270.2559	1
5	9.69	Isopropyl palmitate	142-91-6	C19H38O2	298.2872	1
6	11.33	Imiprothrin (Isomer1)	72963-72-5	C17H22N2O4	318.1580	8
7	11.42	Imiprothrin (Isomer2)	72963-72-5	C17H22N2O4	318.1580	8
8	12.34					
9	12.69	DEHP	117-81-7	C24H38O4	390.2770	6

Molecular composition determination of unknowns

Each mass spectrum of peak No.2 (unknown1) is shown in Figure 3. Although protonated molecule and cationized molecules could not be identified by methane PICI, the ion *m/z 290* obtained by 2% MA could be identified as $[M+CH_3NH_3]^+$. The evidence of Identification is the desorption of methylammonium ($[CH_3NH_3]^+$) from $[M+CH_3NH_3]^+$ by MS/MS (Figure 4).

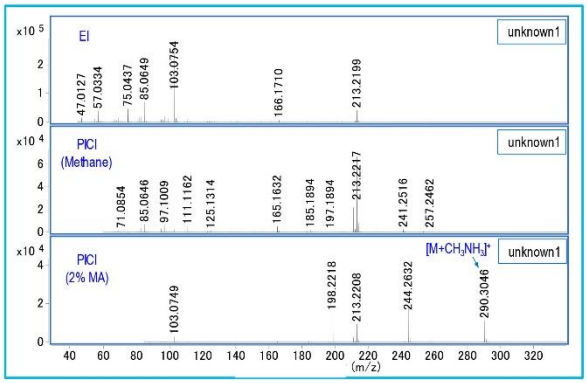

Figure 3. Each mass spectrum of unknown1.

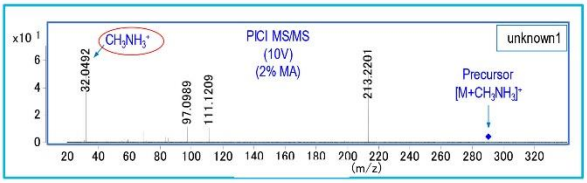

Figure 4. Product ion spectrum of unknown1 obtained by MS/MS of $[M+CH_3NH_3]^+$.

For peak No.8 (unknown2), the ion *m/z 380* could be identified to $[M+CH_3NH_3]^+$ in the same way as unknown1. The mass spectra are shown in Figure 5 and the product ion spectrum is shown in Figure 6, respectively.

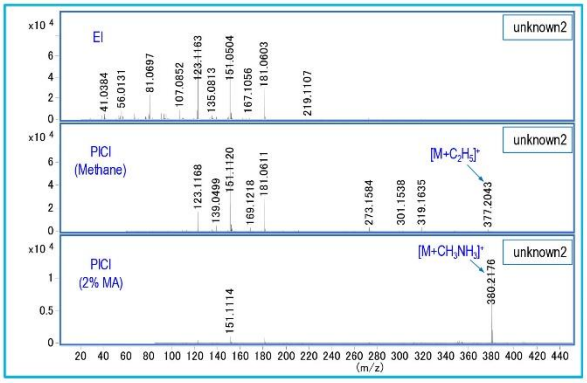

Figure 5. Each mass spectrum of unknown2.

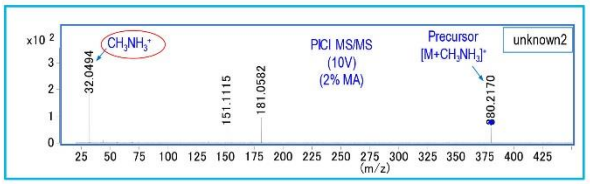

Figure 6. Product ion spectrum of unknown2 obtained by MS/MS of $[M+CH_3NH_3]^+$.

The molecular composition of unknown 1 and unknown2 was calculated to $C_{16}H_{34}O_2$ and $C_{18}H_{24}N_2O_5$ (Table3). The mass error was 2.6ppm and 1.1ppm respectively.

Table 3. Molecular composition of unknown1 and unknown2 calculated from $[M+CH_3NH_3]^+$.

No.	R.T.	Compound	CAS	Molecular fomula	M.W.	DBE
2	7.23	unknown1		C16H34O2	258.2559	0
8	12.34	unknown2		C18H24N2O5	348.1685	8

Molecular structure estimation of unknowns

The molecular structure of unknown1 could be easily estimated from EI mass spectrum to which the fragment ions were assigned (Figure 7).

Results and Discussion

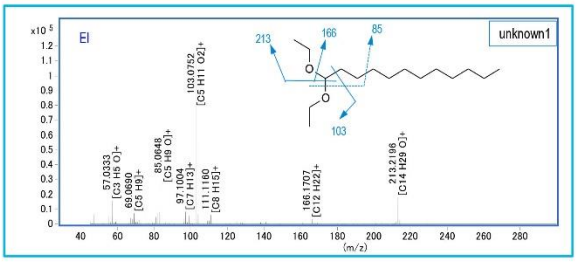

Figure 7. EI mass spectrum of unknown1 and estimated structure.

Unknown2 had a molecular composition close to Imiprothrin. The difference is only CH_2O. The mass spectra had many same fragment ions with Imiprothrin especially on the methane PICI spectrum. The common ions are indicated by blue arrows (Figure 8). The ion *m/z 181* ($[C_8H_9N_2O_3]^+$ indicated by a red arrow is characteristic for unknown2.

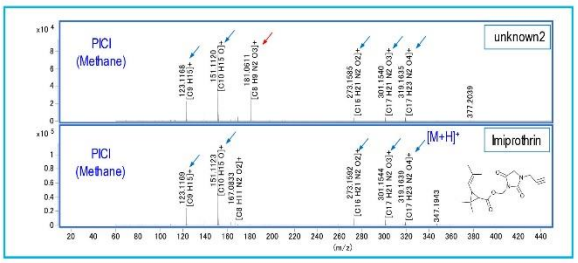

Figure 8. Methane PICI mass spectrum of unknown2 and Imiprothrin.

The product ion spectrum of *m/z 319* obtained from unknown2 was almost perfectly matched with that obtained from $[M+H]^+$ of Imiprothrin (Figure 9). This indicates the structure of unknown2 is partially identical to Imiprothrin.

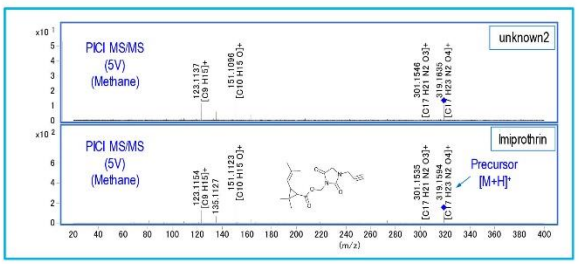

Figure 9. Product ion spectrum of *m/z 319* obtained from unkonwn2 and Imiprothrin.

As shown in Figure 10, the desorption of CH_2O from the ion *m/z 181* ($[C_8H_9N_2O_3]^+$) gives information on the presence of methoxy group and its bonding position. One of the possible structures of unknown2 is shown together in Figure 10.

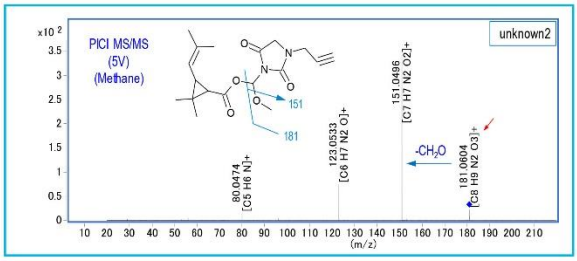

Figure 10. Product ion spectrum of *m/z 181* obtained from unkonwn2.

Conclusions

- As a result of qualitative analysis of insecticide using GC/Q-TOF, seven components out of the nine major components could be identified by library search..
- The molecular composition of the remaining unknown two components was determined by MA PICI and the structure could be estimated using MS/MS.
- Excellent performance of GC/Q-TOF in qualitative analysis was shown

References

1) J.L.Little and A.S.Howard., J. Am. Soc. Mass Spectrom., 24, 1913-1918 (2013)
2) R.Ogasawara and S.Nakamura., The 62th Annual Conference on Mass Spectrometry, Osaka, Japan, (2014)