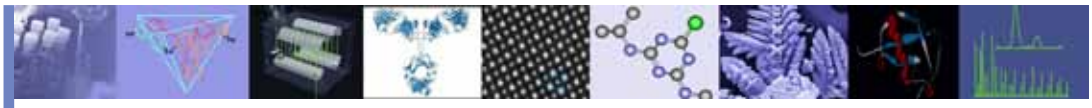

Applications Note

SpiralTOF™

MALDI for Small Molecule Analysis: Triazine Pesticides

Introduction:

Matrix-Assisted Laser Desorption Ionization (MALDI) has been applied to a wide range of analyses and is particularly suitable for the qualitative analysis of high molecular weight samples. On the other hand, MALDI is generally considered unsuitable for low molecular weight compounds because the matrix ions interfere with sample ion detection in the low mass region. However, if these low *m/z* ions can be separated from each other and distinguished with sufficiently high mass resolving power, then MALDI can be expanded to the analysis of low-molecular-weight compounds. We have demonstrated this by using the JEOL MALDI SpiralTOF mass spectrometer The innovative Spiral orbital technology consisting of 4 sets of toroidal electrical sector and Matsuda plates provides ultra-high mass resolving power combined with high ion transmission.

Here we report the use of Spiral technology to collect high mass-resolving power and high mass-accuracy data for eight triazine compounds. Additionally, we report TOF-TOF data obtained with monoisotopic precursor ion selection to provide clear product-ion mass spectra for each compound.

Experimental:

Stock solutions of each of the triazine compounds listed in Table 1 were prepared at concentrations of 1 mg/ml in 2:1 methanol/water. Alpha-Cyano-4-hydroxyxinnamic acid (CHCA, formula = $C_{10}H_7NO_3$) was used as the MALDI matrix. CHCA was dissolved in 1:1 water/acetonitrile containing 0.1% trifluoroacetic acid at a concentration of 10 mg/mL. A 0.5 µL mixture of sample and CHCA (1/1, v/v) was deposited and dried on the MALDI target plate.

The SpiralTOF was operated in positive-ion mode using the full 17-meter flight path. Matrix peaks were used as internal mass reference standards for calibration with the native MS Tornado software.

Results:

(1) SpiralTOF

Accurate mass measurements for the compounds are shown in Table 1.The resolving power (FWHM) for each triazine was approximately 38,000 for the $[M+H]^+$ peak, well in excess of that needed to separate isotope peaks.

Accurate mass values for the protonated molecule of Triazines were determined by using CHCA matrix ions as an internal calibrant. The average mass errors were 0.55 ppm using internal calibration. Mass accuracy and isotopic abundances were sufficient to confirm the elemental composition of protonated molecules.

Table 1. Accurate mass measurement results for protonated molecule of Triazines.

No.	Name	Formula (M+H)	Meas. *m/z*	Error (mDa)	Error (ppm)	Mass resolving power
1	Ametryn	$C_9H_{17}N_5S + H$	228.12774	0.01	0.04	38,361
2	Atrazine	$C_8H_{14}ClN_5 + H$	216.10105	0.04	0.18	37,049
3	Prometon	$C_{10}H_{19}N_5O + H$	226.16624	-0.19	-0.84	36,062
4	Prometryn	$C_{10}H_{19}N_5S + H$	242.14339	0.06	0.24	36,481
5	Propazine	$C_9H_{16}N_5Cl + H$	230.11670	-0.18	-0.78	38,717
6	Simazine	$C_7H_{12}ClN_5 + H$	202.08540	0.21	1.02	37,754
7	Simetryn	$C_8H_{15}N_5S + H$	214.11209	-0.16	-0.73	38,330
8	Terbutryn	$C_{10}H_{19}N_5S + H$	242.14339	-0.14	-0.59	43,185
Average				0.12	0.55	38,242

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(2) TOF-TOF

The TOF-TOF product-ion mass spectra are shown in Figures1-8, and are compared with the corresponding EI mass spectra from the 2011 NIST/EPA/NIH Mass Spectral database. High-energy collision-induced dissociation (CID) mass spectra obtained in the TOF/TOF mode are rich in structurally-significant fragments and show less rearrangement than low-energy CID spectra measured on other types of mass spectrometers. Almost all fragment ions were generated by simple cleavage of chemical bonds by 20 kV high-energy CID.

All of the protonated molecules for the triazines showed a loss of CH_4 (16), *m/z* 15 (CH_3), *m/z* 27 (C_2H_3) and *m/z* 43 (C_3H_7) in the TOF-TOF spectra. Loss of C_3H_6 (42) and loss of C_3H_8N (58) were observed in all of the triazines except simazine, simetryn and terbutryn because these compounds do not have the $NHCH(CH_3)_2$ functional group in their structure. The simazine and simetryn spectra show a losses of C_2H_5 (29) and C_2H_6N (44) from the $NHCH_2CH_3$ functional group. In the atrazine, propazine and simazine mass spectra loss of Cl (35) was observed. Terbutryn showed a loss of C_4H_8 (56) .

Conclusion:

In this study we have demonstrated the potential of TOF/TOF high-energy CID for structural analysis for small molecules.

"SpiralTOF" mode provides

- Ultra high resolving power sufficient to separate analyte ions and matrix ions.
- Routine high mass accuracy (less than 1ppm)

"SpiralTOF-TOF" mode provides

- Monoisotopic precursor selection
- True high-energy (20 kV) CID
- Absence of artifacts from post-source decay (PSD)

Structural analysis of small molecules is easily performed by using the TOF-TOF method. The high-energy CID provided by the JEOL Spiral TOF-TOF produces information-rich structurally significant fragmentation for small molecules that is often directly comparable to EI mass spectra.

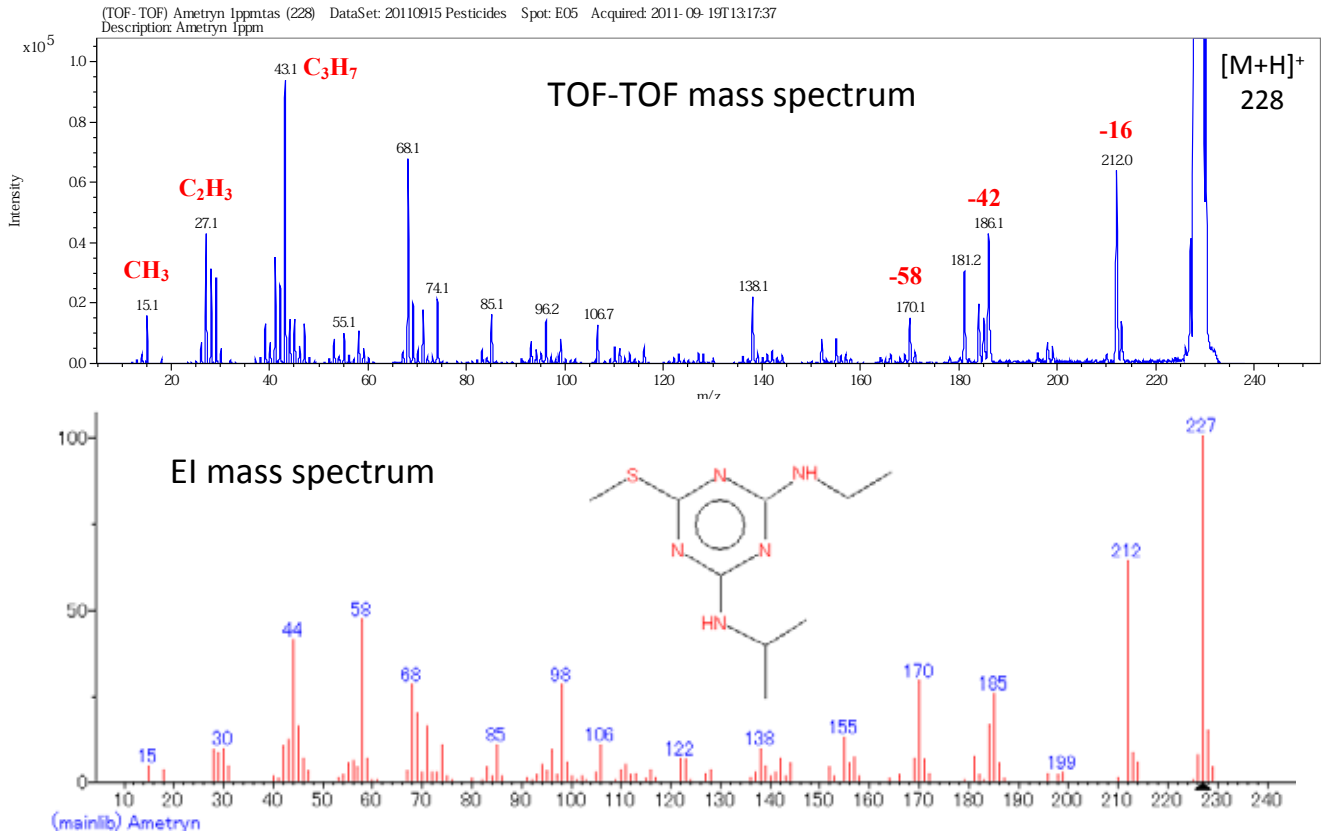

Figure 1. Mass spectra of Ametryn. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

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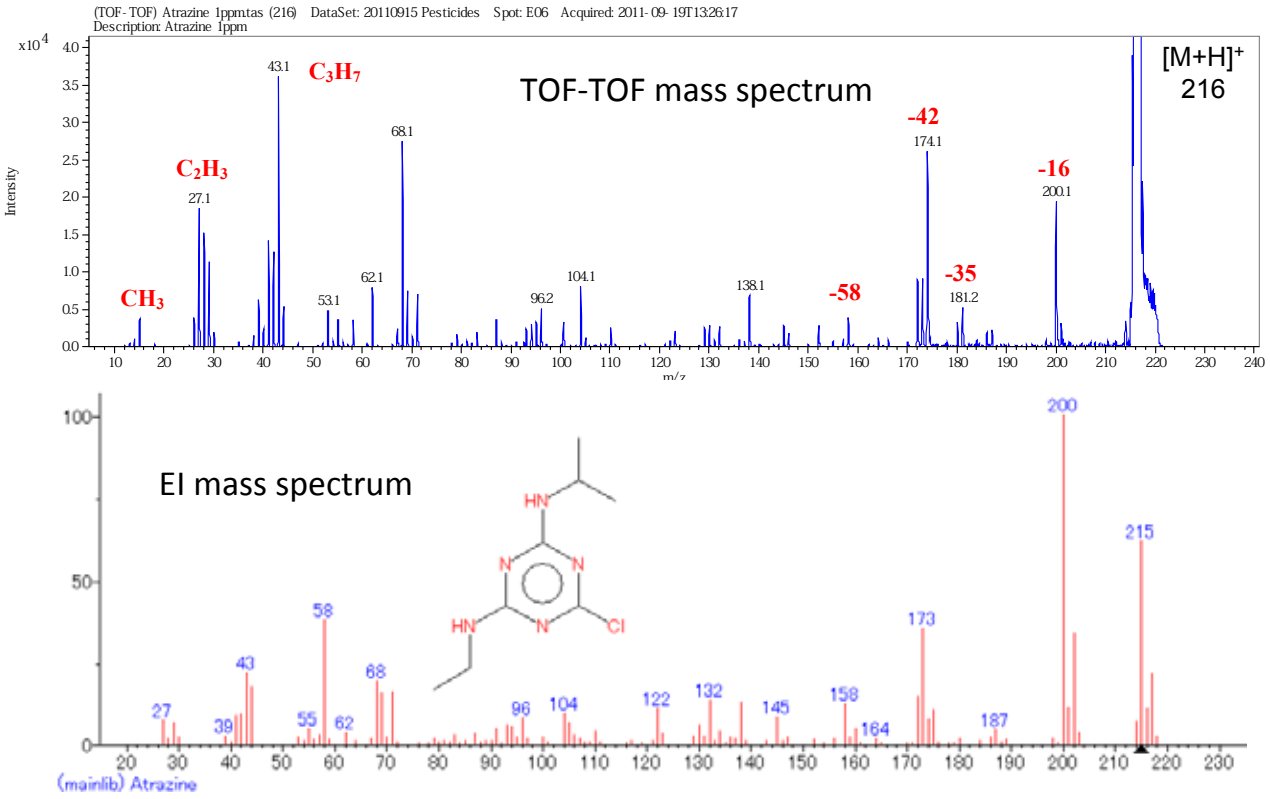

Figure 2. Mass spectra of Atrazine. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

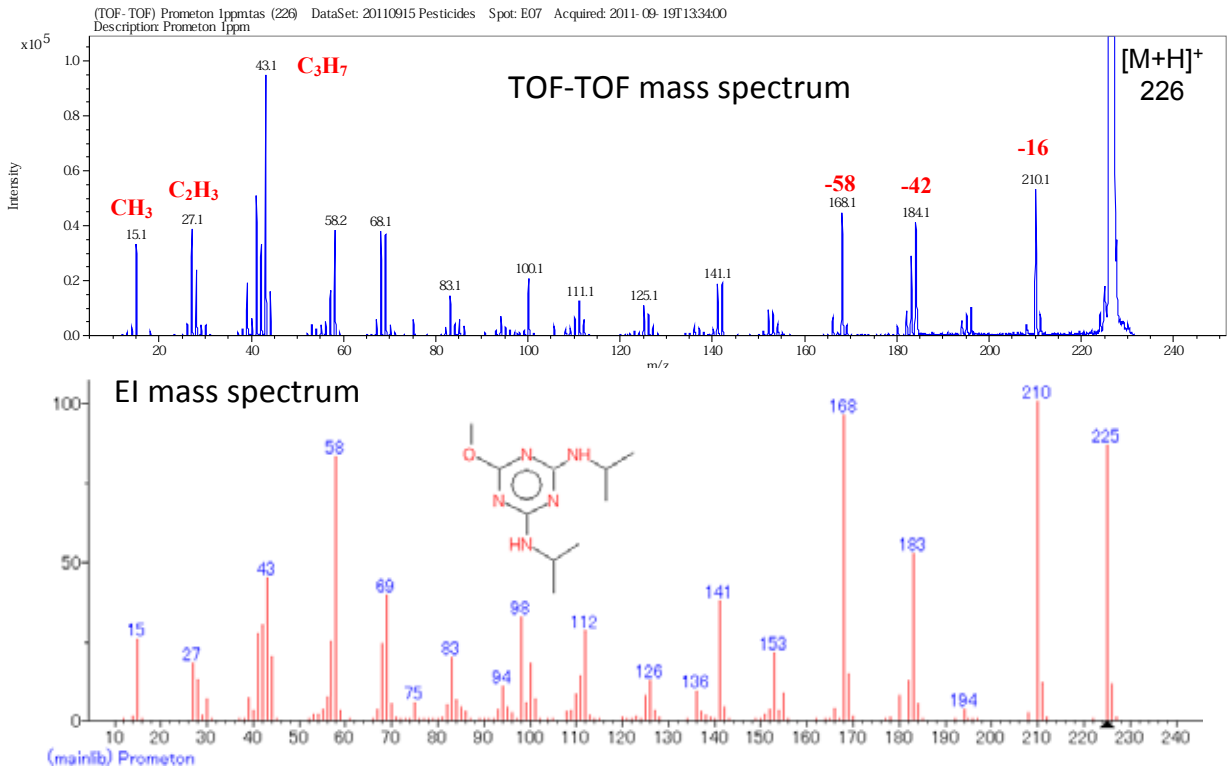

Figure 3. Mass spectra of Prometon. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

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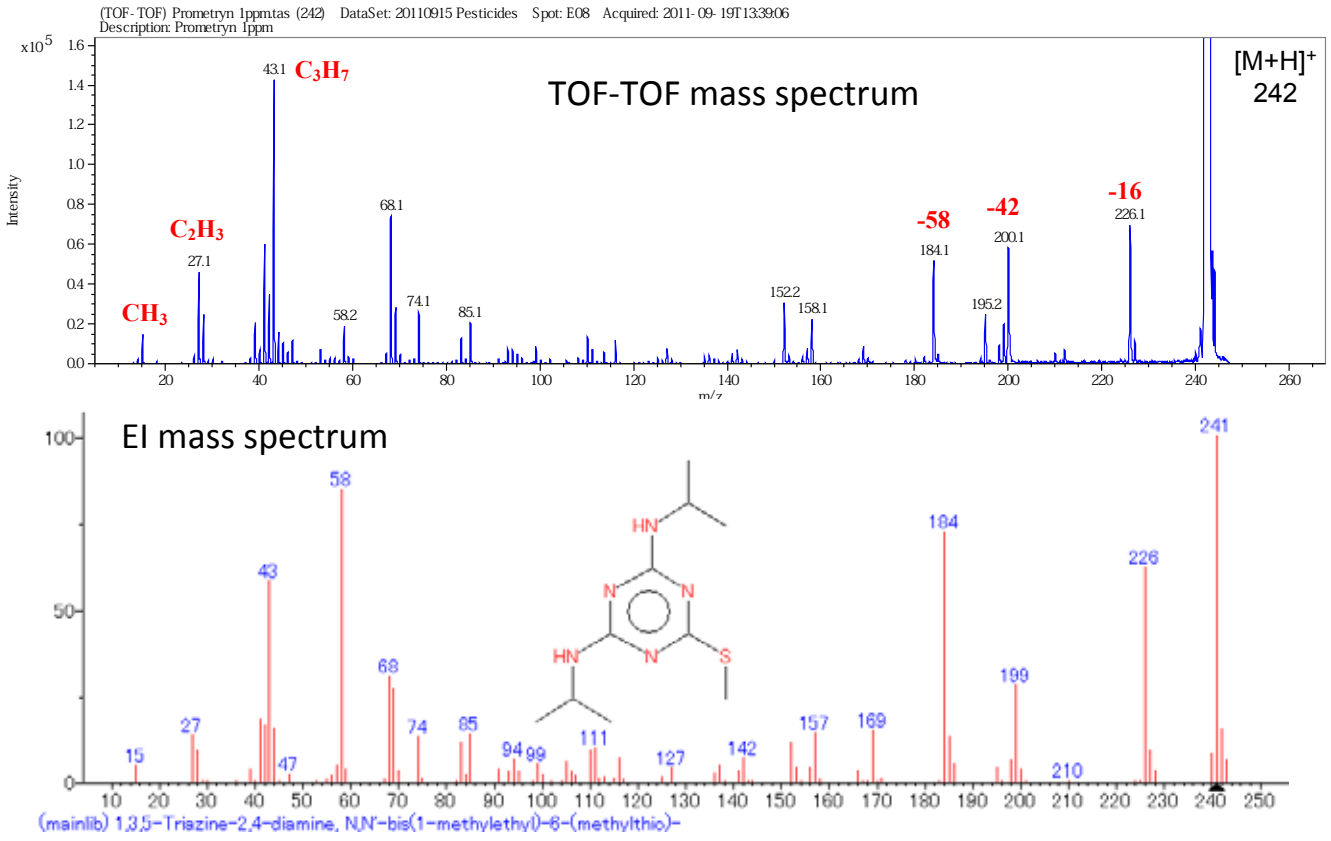

Figure 4. Mass spectra of Prometryn. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

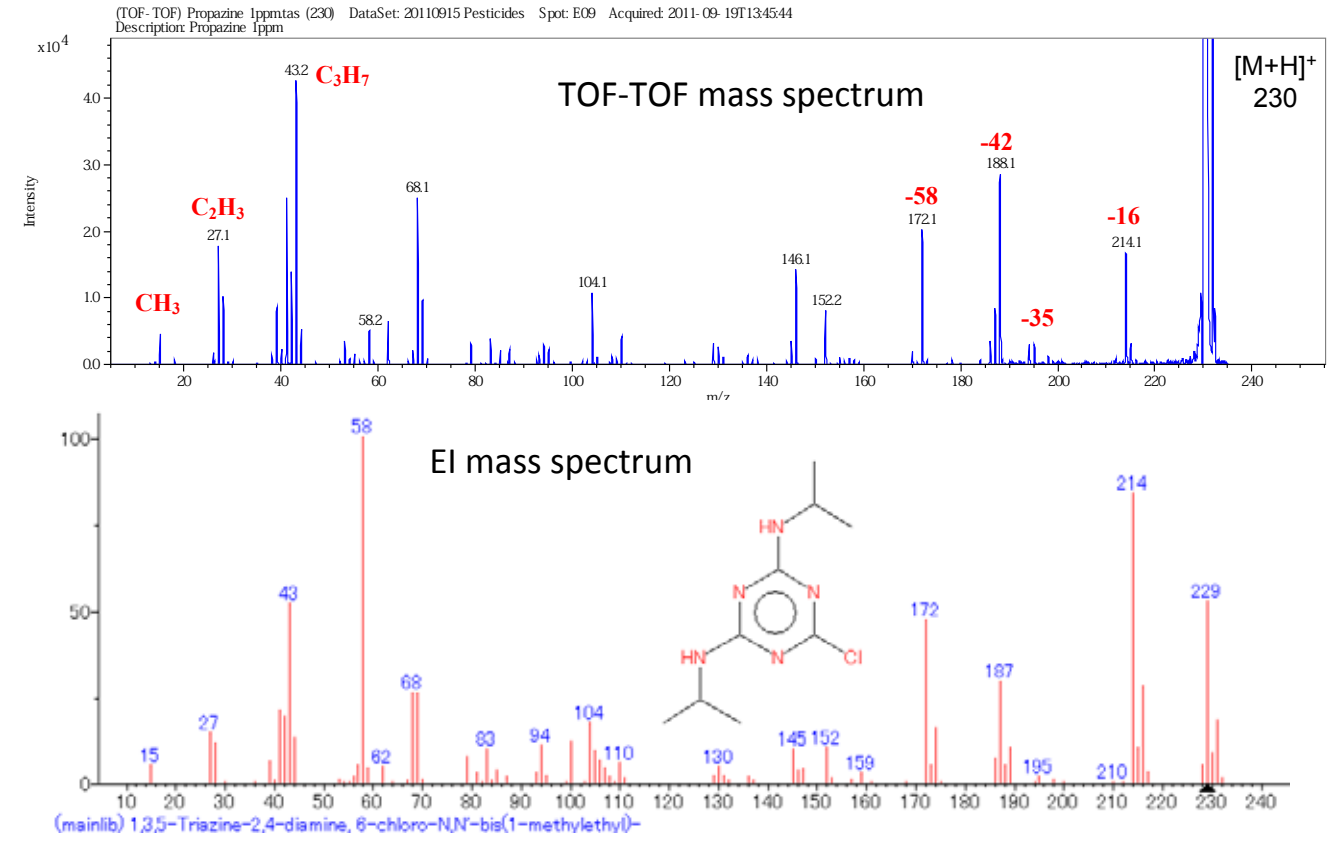

Figure 5. Mass spectra of Propazine. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

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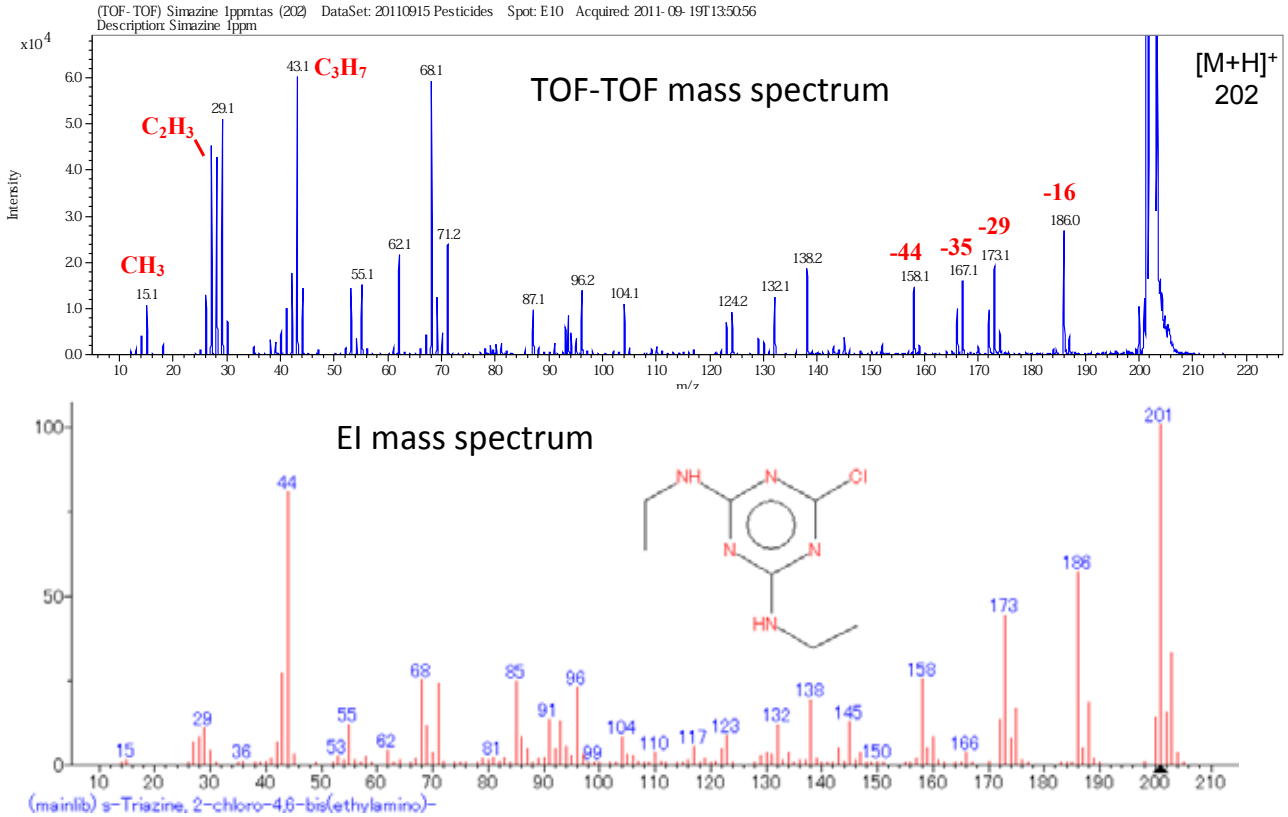

Figure 6. Mass spectra of Simazine. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

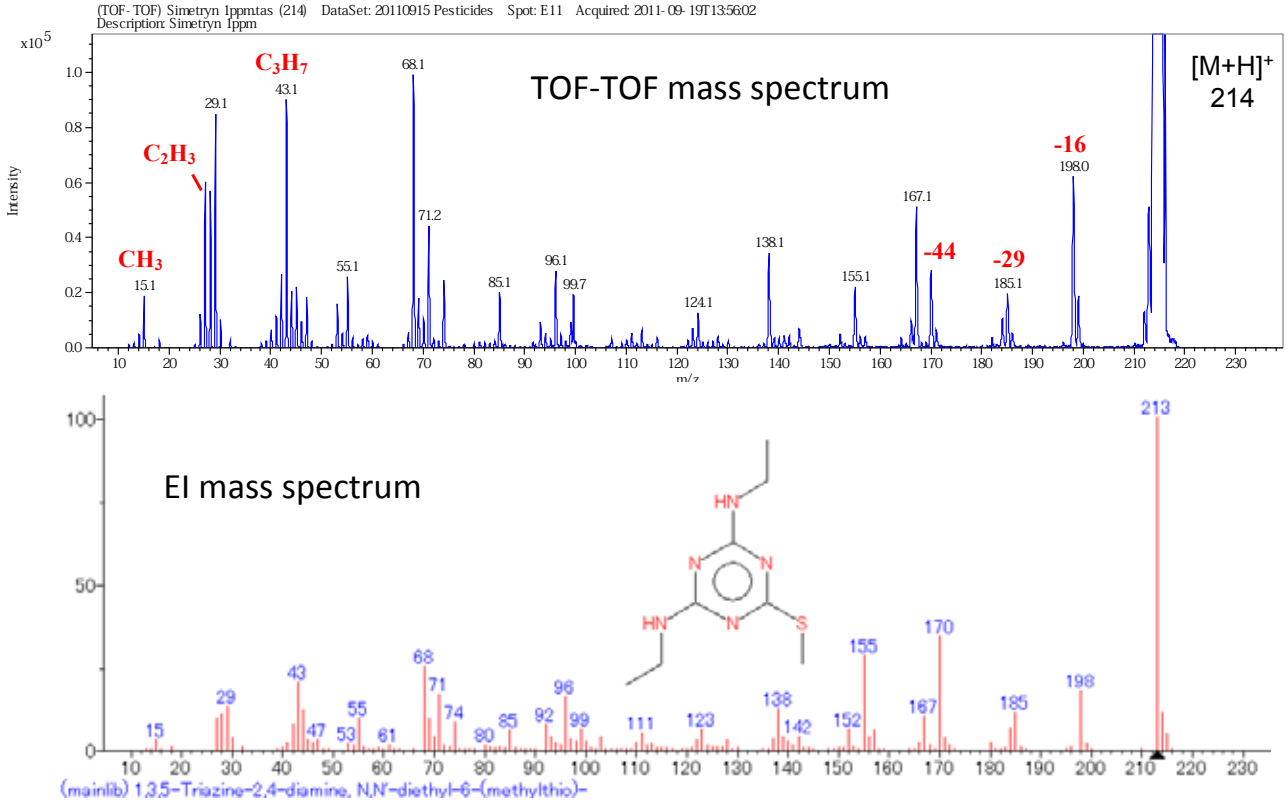

Figure 7. Mass spectra of Simetryn. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

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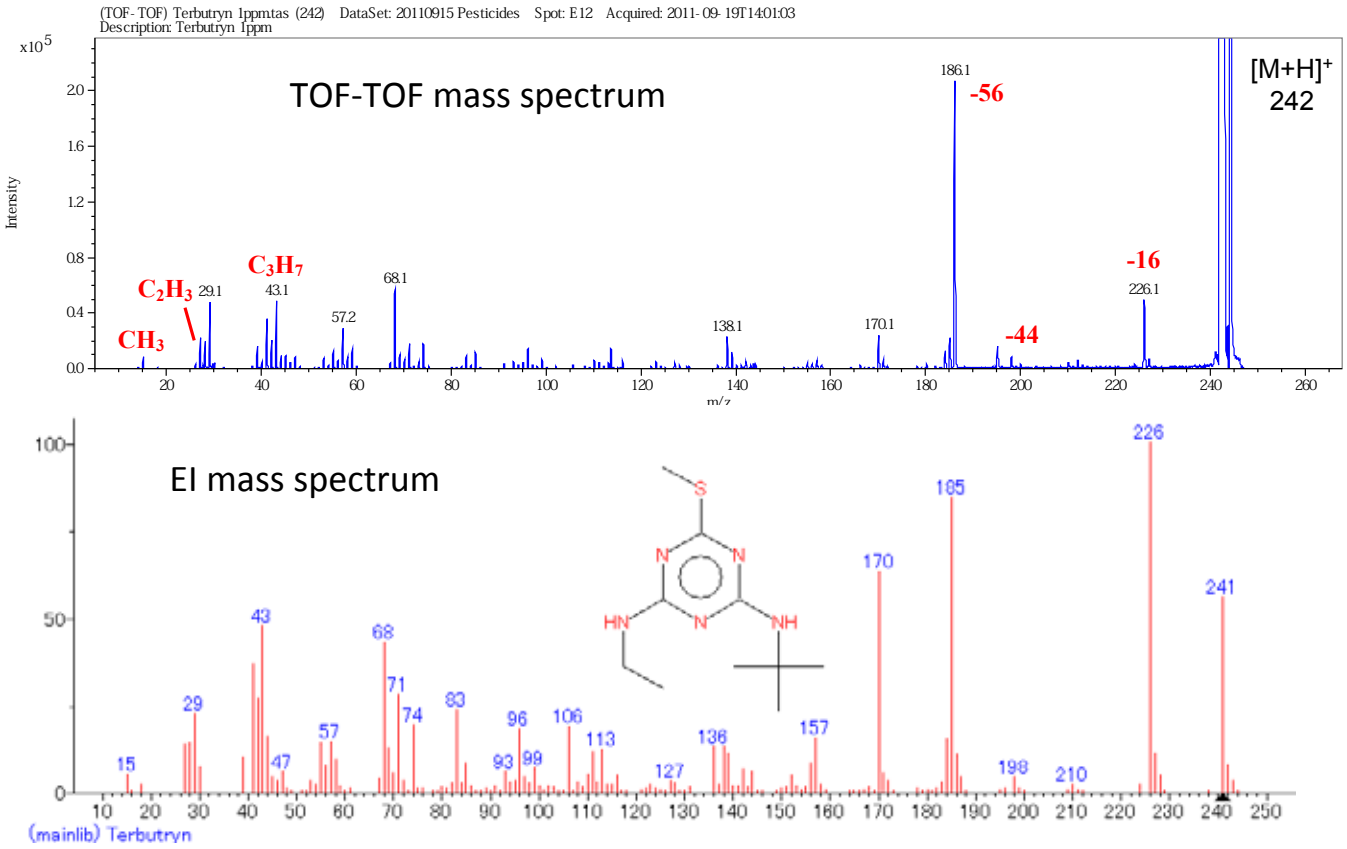

Figure 8. Mass spectra of Terbutryn. Top: MALDI TOF-TOF spectrum Bottom: EI Spectrum

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