

NCI Method Indispensable for GC/MS Measurements of Pesticides

Electron Ionization (EI) Method

GC/MS ionizes compounds and measures their mass numbers. Ionization methods include EI (Electron Ionization) and CI (Chemical Ionization). Typically, the EI method is employed. The EI method produces ions by colliding thermal electrons emitted from a filament with sample gas molecules. This method provides high stability in ionization and the obtained mass spectra show good reproducibility. The EI method provides good results for quantitative analysis as well. Quantitation with GC/MS, in which only ions specific to the compounds are measured, is highly selective analysis method without the affection of interfering components.

This Application News introduces an example of analyzing a pesticide on vegetable (tetradifon), with EI method of GC/MS. Fig. 1 shows the chemical structural of tetradifon, and Table 1 shows the analytical conditions.

Fig. 2 shows the TIC (Total Ion Chromatogram) of a standard sample diluted with a solvent. Peaks for substances other than tetradifon are detected due to hydrocarbons mixed in as interfering components. Fig. 3 shows the EI mass spectrum for tetradifon and Fig. 4 the library search results. The M^+ values (m/z 354, 356 and 358), which indicate molecular weight, are clearly detected.

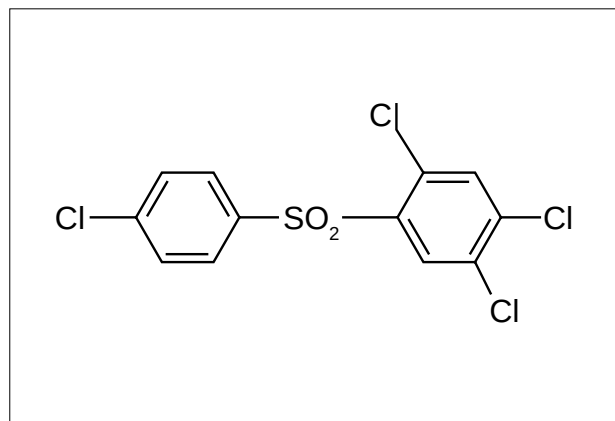


Fig.1 Structure of Tetradifon

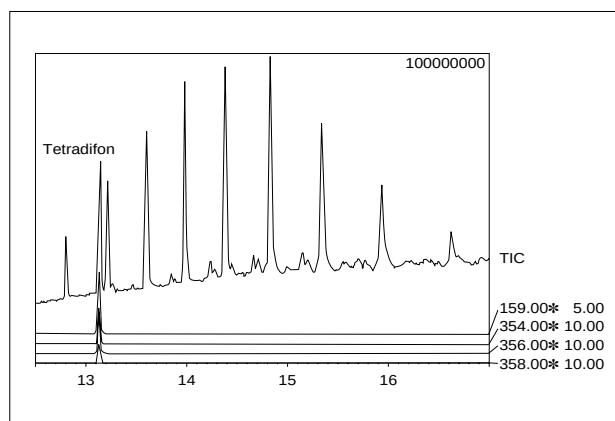


Fig.2 TIC (EI) of Standard Sample (1 ppm)

Table 1 Analytical Conditions	
[GC]	
Column	: (EI) DB-1 30m × 0.25mm I.D. df=0.25μm (NCI) DB-1 30m × 0.25mm I.D. df=0.25μm
Column Temp.	: 50°C (2min) – 20°C/min – 290°C (5min)
He Pressure	: 120 kPa (2min) – 5 kPa/min – 180 kPa (5min)
Injector Temp.	: 280°C
Injection Method	: Splitless (2min)
Injection Volume	: 2μL
[MS]	
Interface Temp.	: 250°C
Scan Range	: (EI) 35–400
Scan Interval	: 0.5sec.
[SIM]	
SIM Ions	: (EI) 159, 229, 356 (NCI) 318, 320
Sampling Interval	: 0.2sec.

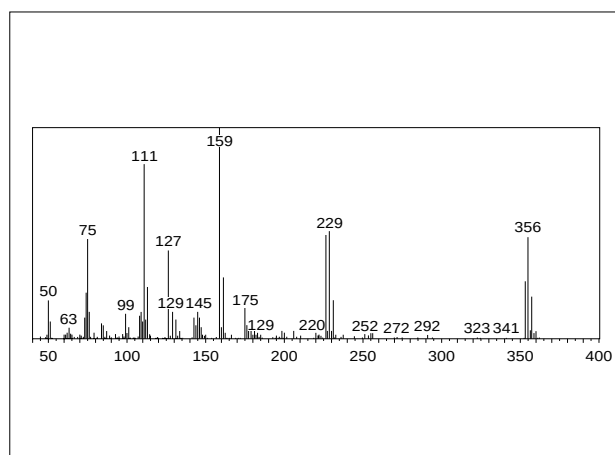


Fig.3 EI Mass Spectrum of Tetradifon

Fig. 5 shows the TIC for a cucumber extract. A major peak is detected at 13.13 minute, where tetradifon is expected to appear. Fig. 6 shows the mass spectrum for the peak, and Fig. 7 the library search results. The result shows that the peak is a type of fatty acid ester. However, characteristic ions of tetradifon at m/z 159, 354, 356 and 358 are also detected.

Then SIM measurement was performed to further increase quantitative accuracy. Fig. 8 shows the measurement result for a 1 ppb concentration standard sample, and Fig. 9 the calibration curve for 1 ppb - 1000 ppb range. Good linearity is obtained. Fig. 10 shows the SIM chromatogram the cucumber extract. Tetradifon is detected without being affected by interfering substances.

Thus, even when interfering components exist in the sample, GC/MS achieves accurate measurement of target substances by measuring specific mass numbers.

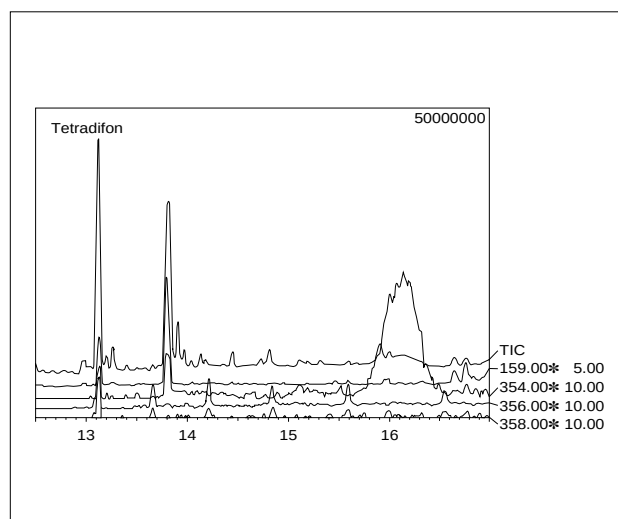


Fig.5 TIC (EI) of Cucumber Extract

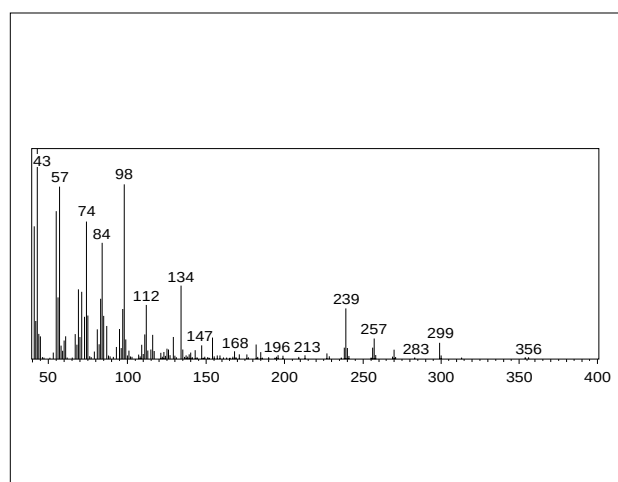


Fig.6 Mass Spectrum (EI) of Cucumber Extract

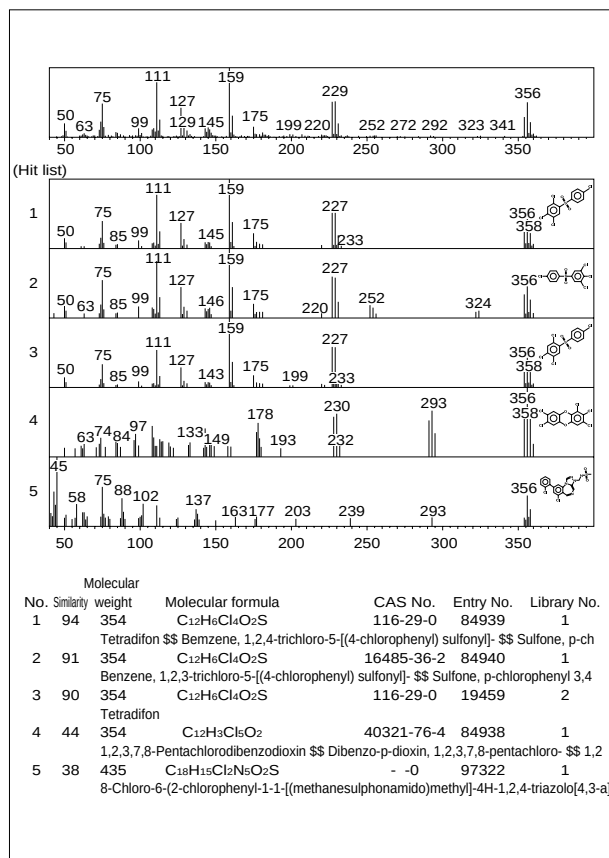


Fig.4 Library Search Results (EI)

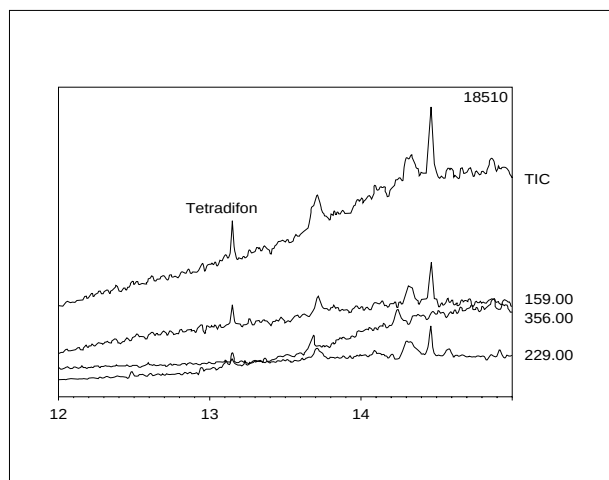


Fig.8 SIM (EI) of Standard Sample (1 ppb)

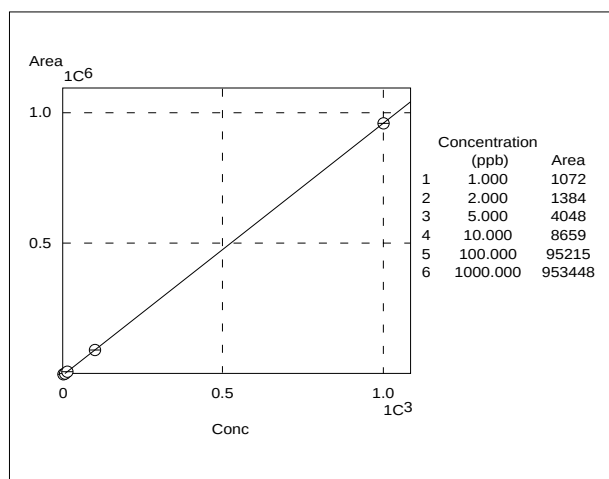


Fig.9 Calibration Curve (EI) for Standard Sample (1 - 1000 ppb)

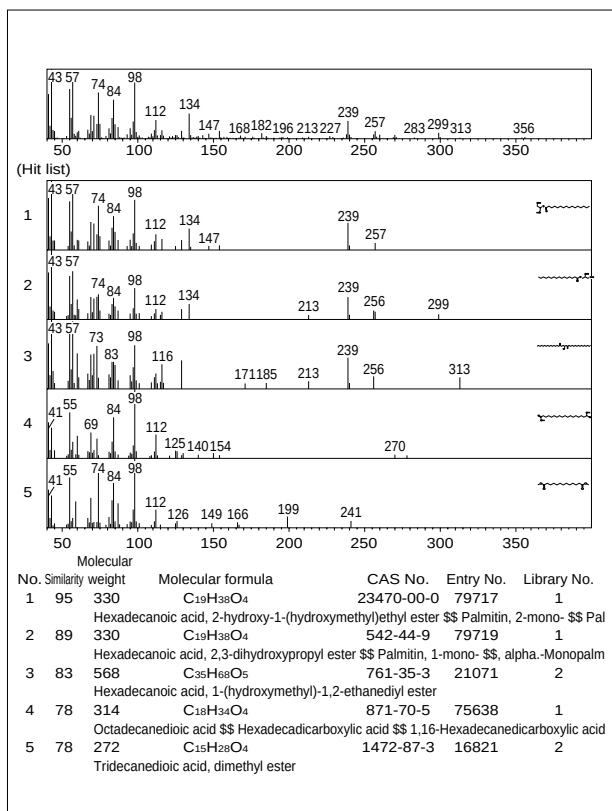


Fig.7 Library Search Results (EI)

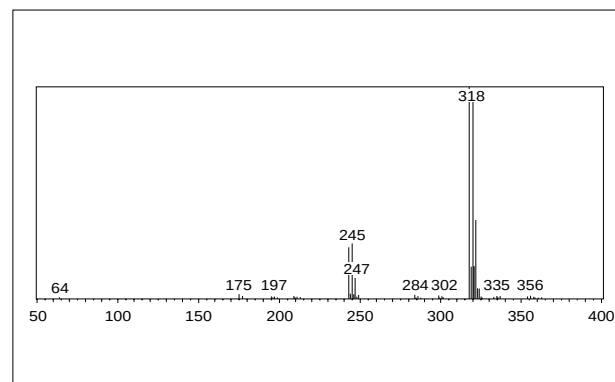


Fig.12 Mass Spectrum (NCI) of Tetradifon

Negative Chemical Ionization (NCI) Method

CI (Chemical Ionization) is one of the methods to ionize compounds by introducing a reagent gas, such as methane, isobutene and ammonia, to ion source. In this method, the sample is ionized via molecular reaction between the sample and the reagent gas ions, or electron capture process which is a major process producing negative ions.

The produced ions include positive (+) ions and negative (-) ions. Accordingly, the CI method is divided into two types; positive chemical ionization (PCI) and negative chemical ionization (NCI). NCI is characterized by measurement with high sensitivity and quantitation with high selectivity for high electron affinity compounds.

The TIC spectrum of a standard sample using NCI is shown in Fig. 11 and the mass spectrum in Fig. 12. Hydrocarbons, which were detected with EI method, are not detected with NCI method. The reason is because negative ions do not generate from hydrocarbons. The (M - Cl) ions of m/z 318, 320 and 322 are detected in the mass spectrum. A TIC of the cucumber extract is shown in Fig. 13 and the mass spectrum for the position where tetradifon should appear is shown in Fig. 14. A mass spectrum identical to the standard sample is obtained, without any interference.

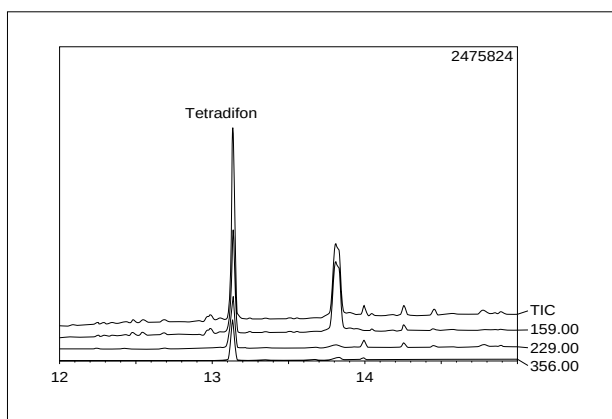


Fig.10 SIM (EI) of Cucumber Extract

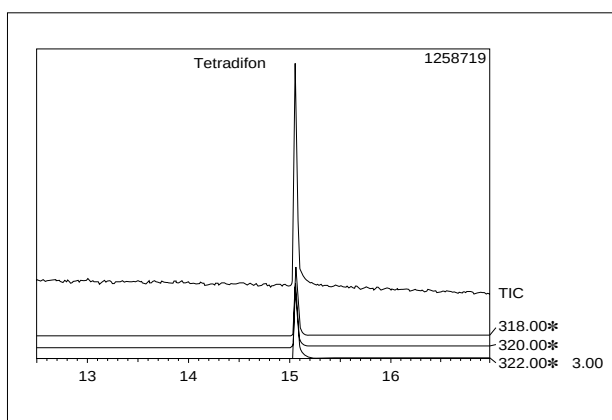


Fig.11 TIC (NCI) of Standard Sample (1ppm)

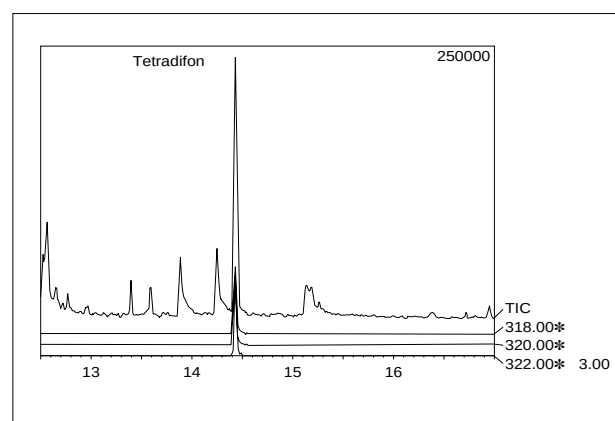


Fig.13 TIC (NCI) of Cucumber Extract

SIM measurements were also performed. The SIM results for 1 ppb, 2 ppb and 10 ppb standard samples are shown in Figs. 15-1, 15-2 and 15-3, respectively. Fig. 16 shows the calibration curve for 1 - 100 ppb. A detection sensitivity 100 times higher than that of the EI method, and good linearity were achieved. Fig. 17 shows the chromatogram for the cucumber extract. A clear chromatogram without any affection of interfering components was obtained.

As demonstrated here, the NCI method achieves selective analysis of target substances without being affected by interfering substances and its sensitivity is probably 100 times higher than that of the EI method.

Thus the NCI method is indispensable for GC/MS analysis for pesticides in food products and vegetables.

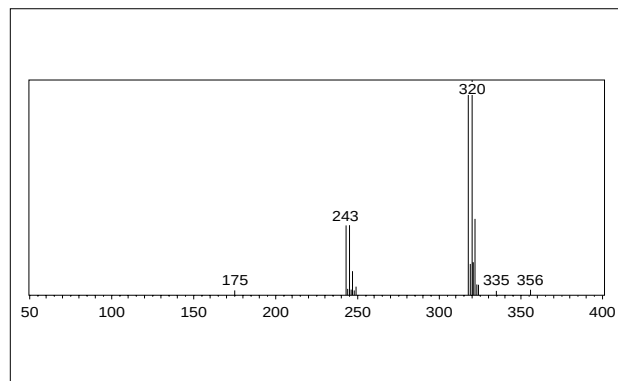


Fig.14 Mass Spectrum (NCI) of Cucumber Extract

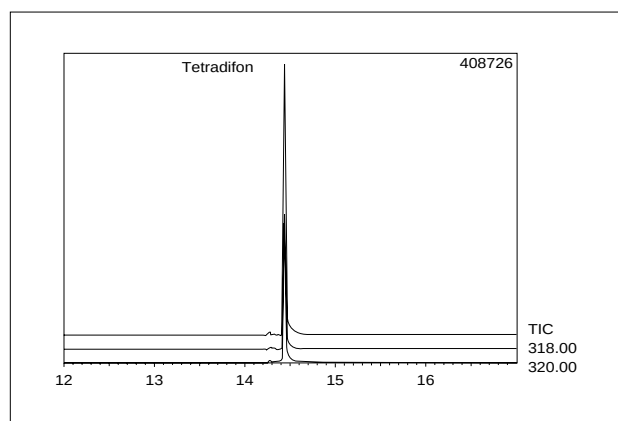


Fig.17 SIM Chromatogram (NCI) of Cucumber Extract

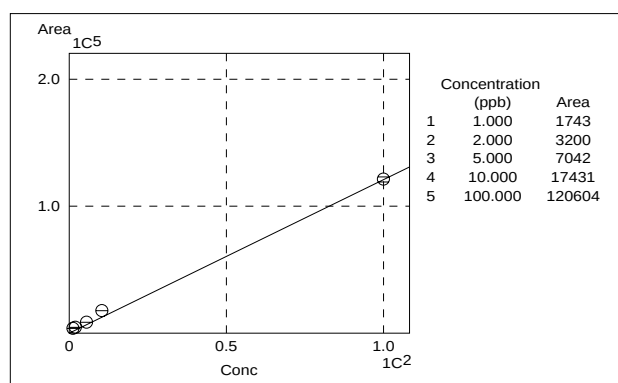


Fig.16 Calibration Curve (NCI) for Standard Sample (1 - 100ppb)

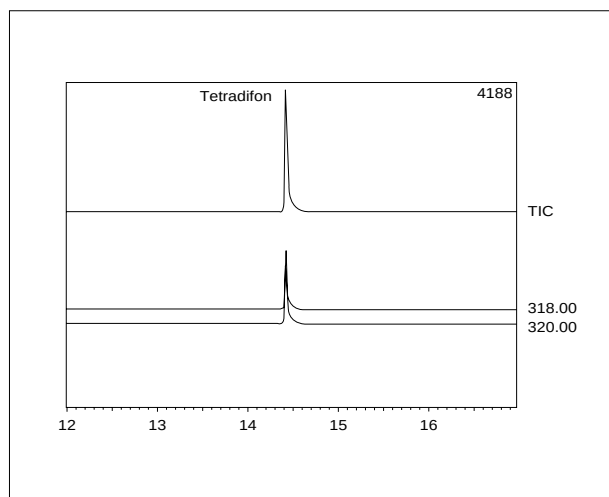


Fig.15-1 SIM Chromatogram (NCI) of Standard Sample (1ppb)

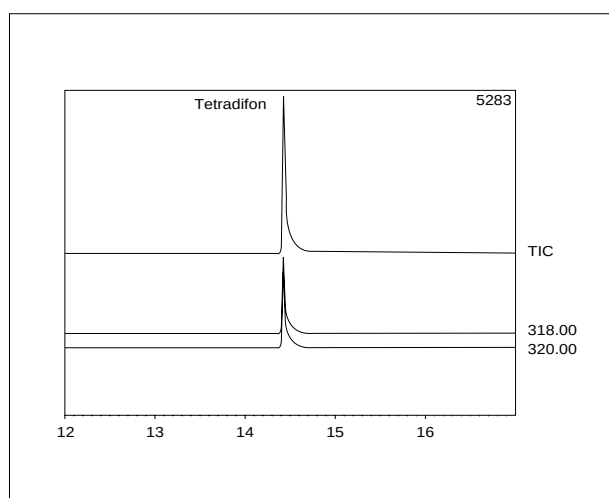


Fig.15-2 SIM Chromatogram (NCI) of Standard Sample (2ppb)

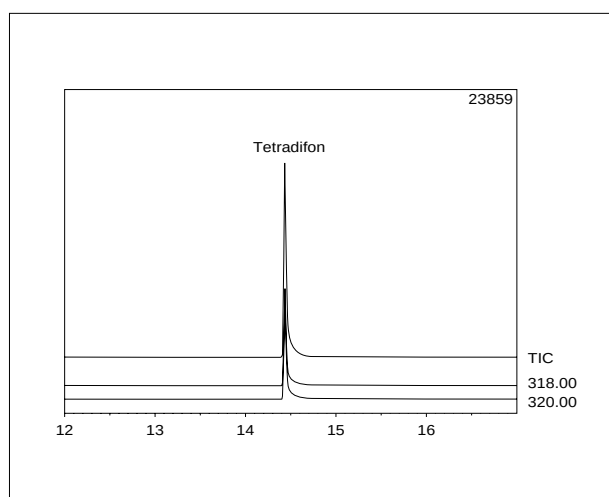


Fig.15-3 SIM Chromatogram (NCI) of Standard Sample (10ppb)