

ANALYSIS OF RESIDUAL AGRICULTURAL CHEMICALS IN WINE USING GC/MS

Methylisothiocyanate (MITC) is used as a bactericide in soil. Recently, this pesticide was found present in Italian wine, creating a consumer problem. MITC is normally analyzed using GC, but due to the effect of impurities, etc., identification is difficult by this method. Introduced here is the analysis of MITC using GC/MS, an excellent method for conducting qualitative analysis.

Since identification via GC/MS is based on both the chromatographic retention times as well as mass numbers obtained from mass analysis, identification reliability is enhanced.

For the sample, a commercial MITC standard sample was diluted using ethyl acetate. Figure 1 shows a mass chromatogram of the sample at 20ppm. Figure 2 shows

the associated mass spectrum, and Figure 3 shows the library search result. From Figure 2, the MITC molecular ion (M^+ : m/z 73) is effectively detected, and m/z 36 and 45 fragment ions are also seen. The mass numbers of these fragment ions together with the ratio of the ion heights (pattern coefficient, or isotopic ratio) enable identification of the component.

For quantitative analysis, selected ion monitoring (SIM) is used. Using this method, only the ion(s) unique to the target compound are detected. Identification of the peaks necessary for performing quantitative analysis is performed using the retention time and mass number(s), and quantitation is performed using the peak height or peak area.

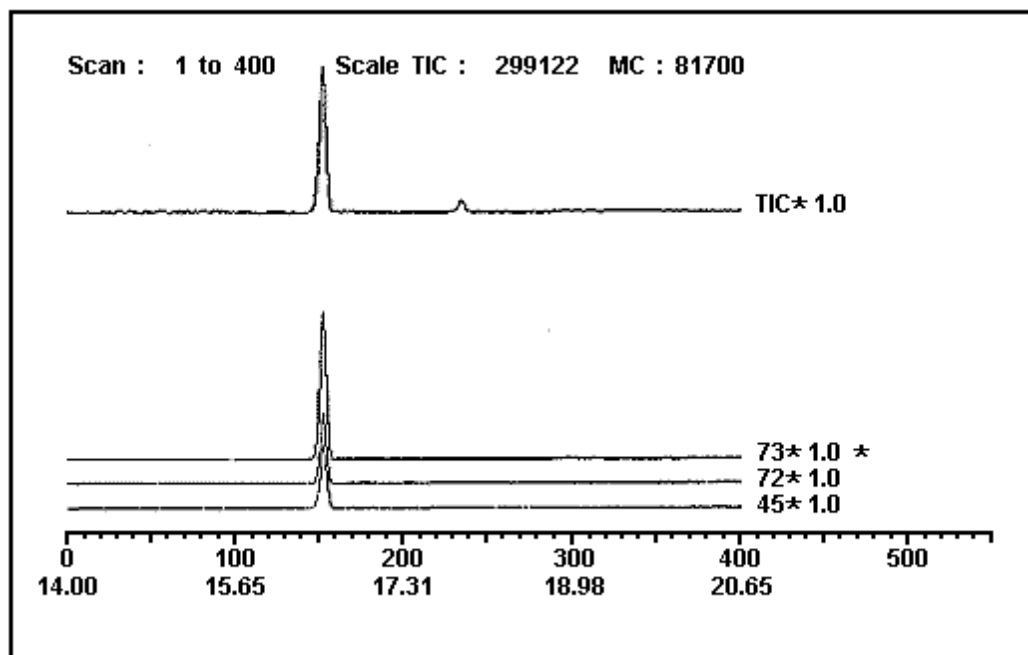


Figure 1 – MITC Mass Chromatogram (10ppm)

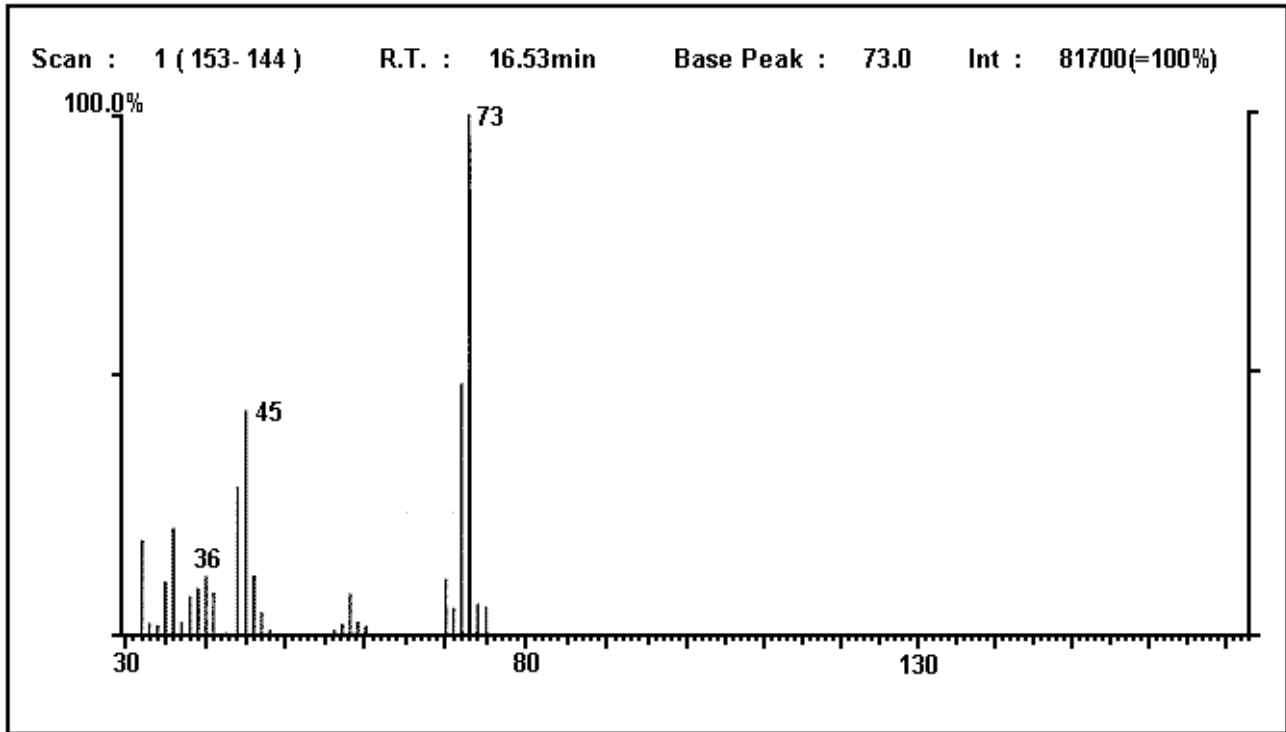


Figure 2 – Mass Spectrum of Methylisothiocyanate

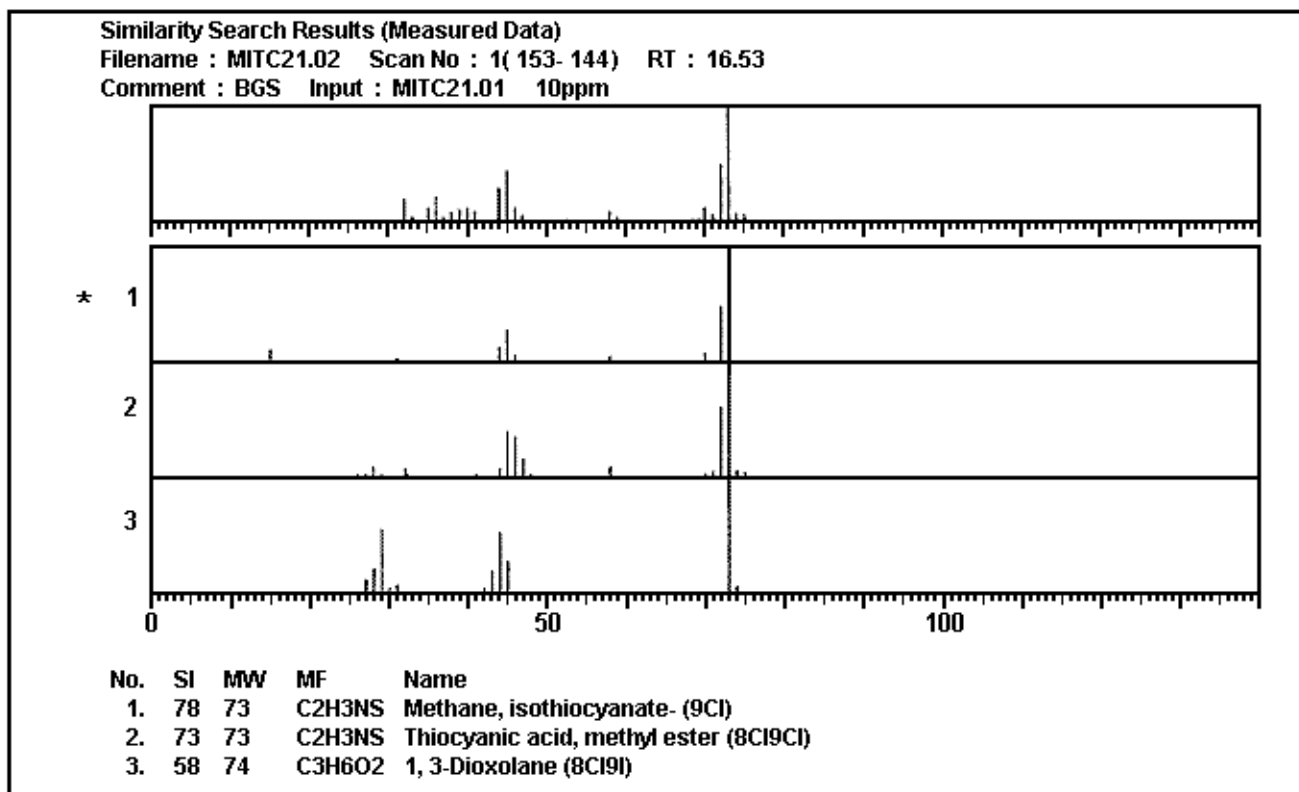


Figure 3 – Library Search Result for Methylisothiocyanate

Column : CBJWAX-S60-050 (60 m X 0.32 mm, df=0.5 μm)

Column Temp. : 50°C —^{3°C/min}→100°C —^{10°C/min}→150°C
 (1min)

Injection Temp. : 250°C

Ion Source Temp. : 250°C

Electron Energy : 70eV

Methylisothiocyanate (MITC)
 $\text{CH}_3\text{—N=C=S}$ Molecular Weight (73)

Table 1 – Analytical Conditions

Figures 5 through 7 show the SIM chromatograms for m/z 45, 72 and 73, at sample concentrations of 20ppb, 100ppb and 500ppb, respectively. In addition, Figure 4 shows the calibration curve generated from the peak areas based on

the chromatogram for the m/z 73 ion. Figure 8 shows the SIM chromatogram of the wine extracts with added MITC standard spiking. Based on the calibration curve, the calculated concentration of MITC was 100.5 ppb.

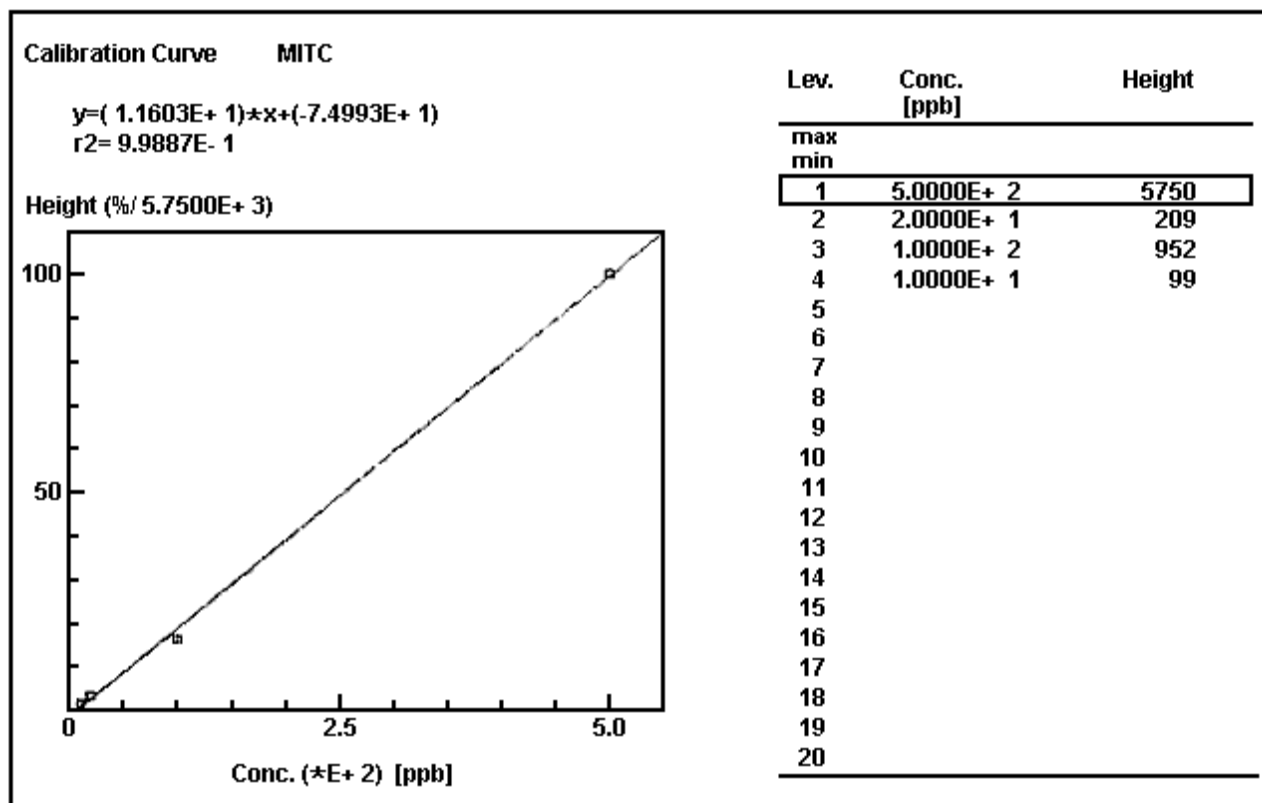


Figure 4 – Calibration for Methylisothiocyanate

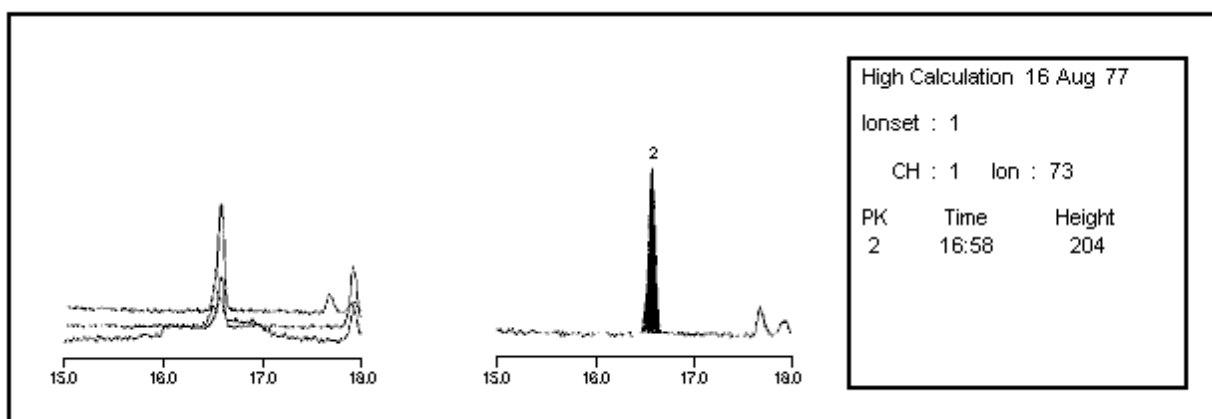


Figure 5 – Selected Ion Chromatogram (20ppb)

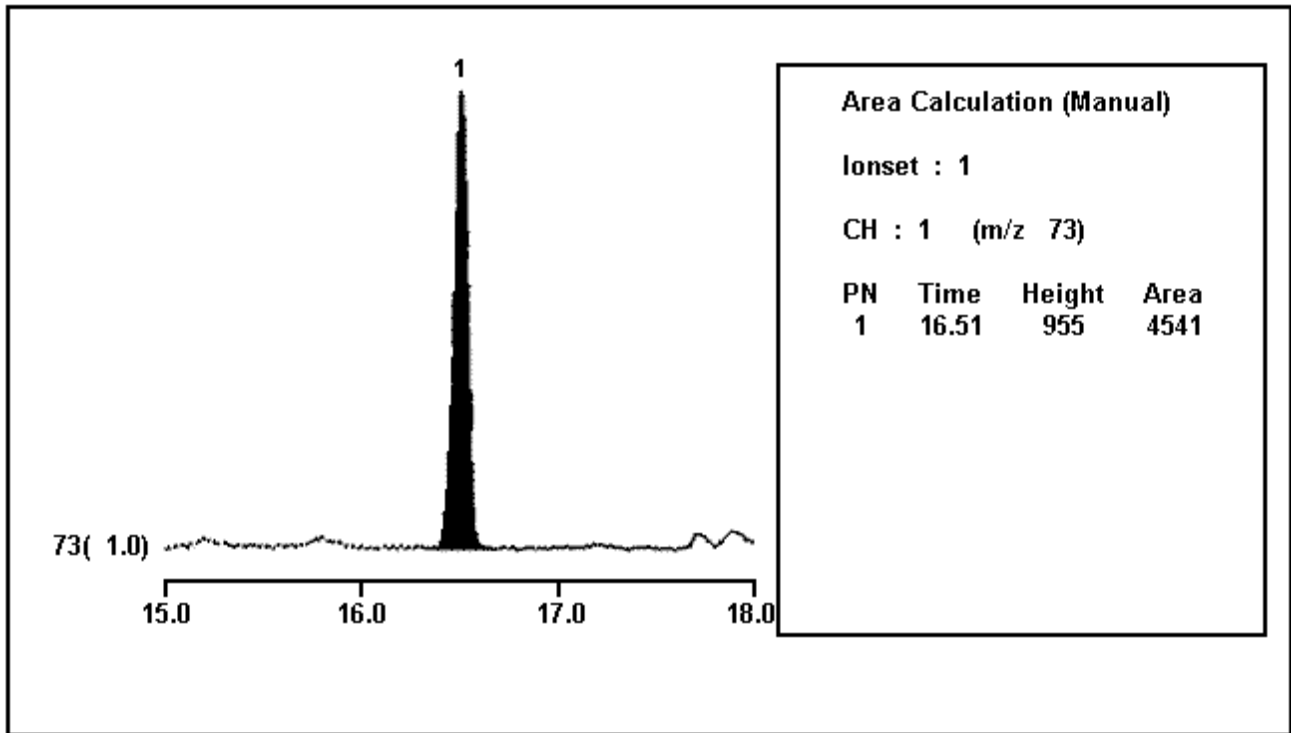


Figure 6 – Selected Ion Chromatogram (100ppb)

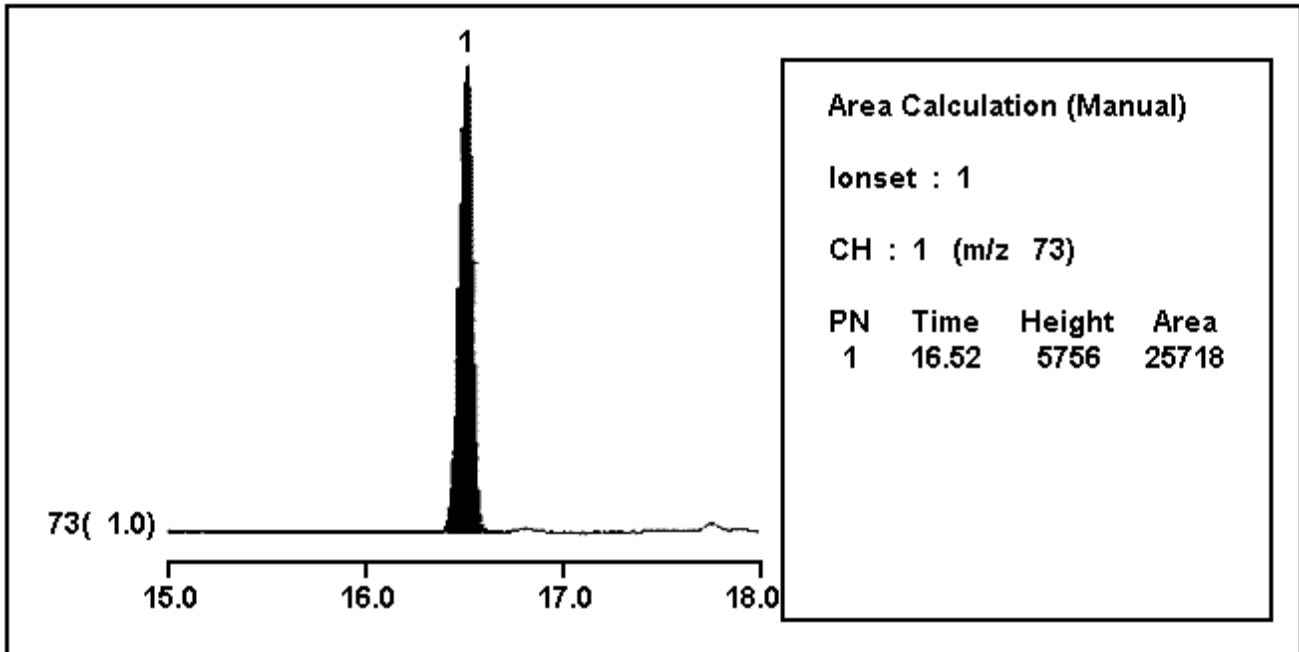


Figure 7 – Selected Ion Chromatogram (500ppb)

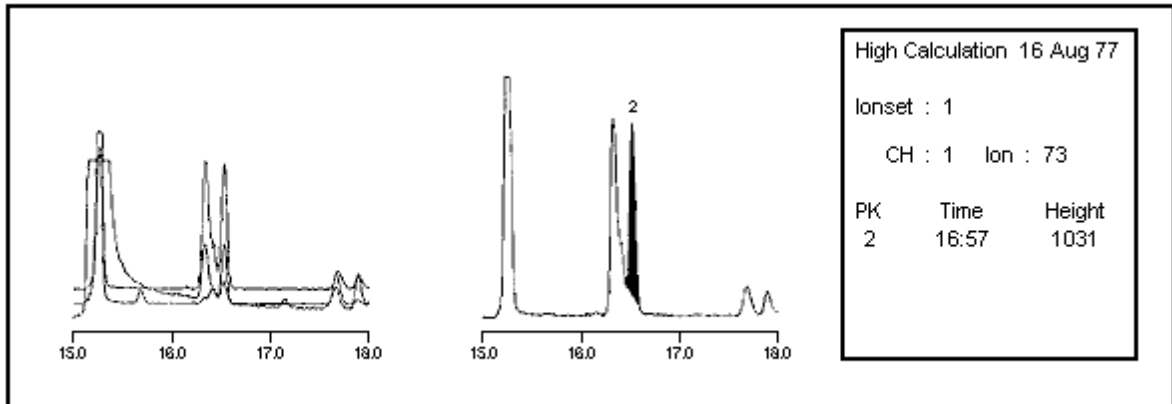


Figure 8 - Selected Ion Chromatogram (extracts)