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Identification of Triallate in Grain Pellets

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Primary methods of analysis of pesticide residues used in this laboratory are well documented in the PESTICIDE ANALYTICAL MANUAL (1982). In addition, our techniques also involve acetone extraction and dichloromethane partitioning followed by gas chromatography (GC) on various stationary phases with different detectors (LUKE et al. 1975, 1981). Increased utility of gas chromatography-mass spectrometry (GCMS) to provide structural elucidation of unidentified analytical responses (UARs) encountered during such an analytical approach has become well established (CAIRNS et al. 1983). However, the dramatic change in elution profiles from using a specific detector to MS detection can cause problems. Perhaps the most notable is the impaired ability to detect the compound of interest among so many other possible procedural contaminants and background components. The key to a successful identification must rely heavily on the proper transition from GC to GCMS in terms of relative retention times.

This paper describes the identification of a UAR (found to contain N, S and Cl) in grain pellets to be the herbicide, triallate [S-(2,2,3-trichloro--2-propenyl)bis(1-methylethyl)carbamothioate].

MATERIALS AND METHODS

Mass Spectral Data. All spectra were obtained on a Finnigan Model 3300 quadrupole mass spectrometer equipped with a CI source and INCOS Data System; operating conditions: 150 cm x 2 mm i.d. glass column packed with 3% OV-17 on 80/100 mesh Chromosorb W; carrier gas and reagent gas, 30 mL methane/min; column inlet, 250°C; column temperature, 200°C, isothermal.

Sample Preparation. Three 100 g portions of the sample were extracted by sec. 212.13b of the PESTICIDE ANALYTICAL MANUAL (Volume 1, 1982), and eluted through Florisil using eluate II of sec. 252 of the PESTICIDE

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ANALYTICAL MANUAL (Volume 1, 1982) and concentrated to dryness using a stream of dry nitrogen and then diluted to 200 uL with acetone; 3 uL of this extract representing 0.9 g of sample was then used for analysis.

RESULTS AND DISCUSSION

The sample extract was first examined under CI methane GCMS conditions (Fig. 1). From a precursory review of the total ion chromatogram (Fig. 1A), the high incidence of detection of constituents other than the one of interest can be rationalized in terms of the MS behaving like an FID detector, i.e. non-specific. Since the UAR in question should have eluted at approx. 2.6 min, a more detailed examination of that time zone did reveal the presence of a compound with a strong ion at m/z 128. This ion contained no evidence to suspect a chlorine content. A mass chromatogram constructed from searching the total ion profile for m/z 128 (Fig. 1B) clearly illustrated the presence of the compound. Having now recognized the retention time of the UAR,

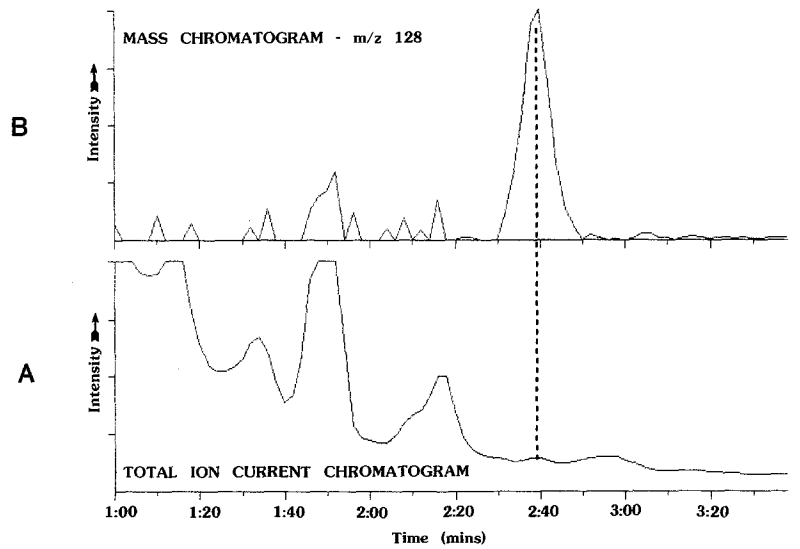


Figure 1. Mass spectral data obtained from extract of grain pellets: **A**, total ion chromatogram (m/z 80-350) under methane CI conditions; **B**, mass chromatogram for m/z 128.

its mass spectral characteristics were then obtained using both ammonia and methane as reagent gases under CI conditions (Fig. 2A,B). The appearance of an ion at m/z 304 could have corresponded to MH^+. This ion did contain an isotopic cluster at m/z 304, 306, and 308

indicating the presence of three chlorine atoms. Since the base peak at m/z 128 did not contain any chlorine atoms, then it must have resulted from a fragmentation pathway with loss of that portion of the molecule which did contain the three chlorines. However, to obtain the m/z 128 ion, a loss 176 mass units (m/z 304 - m/z 128) would be necessary to accommodate this primary proposal. Assuming the three chlorines were lost

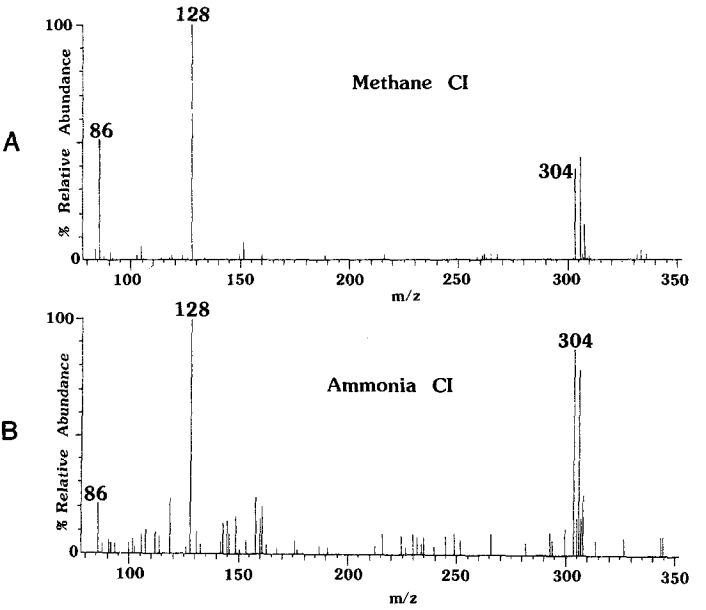
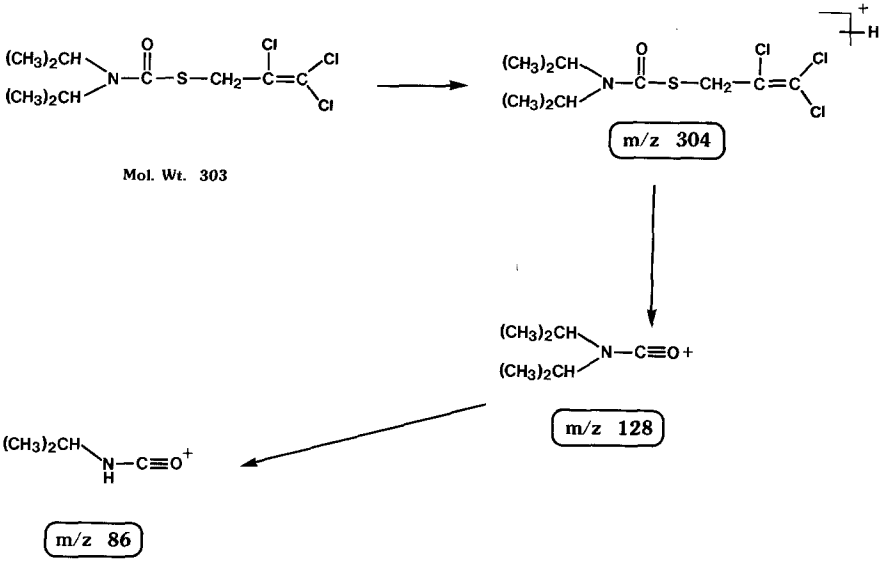


Figure 2. Mass spectra of triallate recorded under CI conditions: A, methane; B, ammonia.

together with C_3H_4, then the remaining atoms to be accounted for would have an approximate molecular weight of about 30. These rough calculations then led to the basic resolution that the sulfur atom (known to be present from specific GC work) was also lost with that portion of the molecule containing the three chlorines, i.e. $-SC_3H_2Cl_3$. The presence of the ion at m/z 128 has already been observed with thiocarbamates (THOMPSON et al. 1966; BENSON & DAMICO 1968) as the di-n-propylisocyanate ion. Since the UAR exhibited an ion at m/z 128 containing N, the strong possibility existed that the compound was a thiocarbamate. Additionally, the appearance of an ion at m/z 86 could correspond to the loss of C_3H_6 from the m/z 128 ion. With these preliminary deductions based solely on low resolution measurements, it was concluded that the compound could be triallate. A reference standard was obtained and the hypothesis was confirmed. The

fragmentation pathway was then proposed to occur as illustrated in Scheme 1. It is interesting to note that the protonation of triallate can occur both with ammonia and methane. Normally, the loss of HCl is experienced after protonation (CAIRNS et al. 1982). Formation of the isocyanate ion (m/z 128) as the base peak is not surprising in that the same ion was the dominant species in the EI spectra of thiocarbamates (BENSON & DAMICO 1968). What is unusual about this finding is that it is the first incidence of triallate in grain pellets we have encountered. Residues of diallate (the corresponding dichloro compound) have been found on a semi-regular basis. Although the toxicity [acute oral LD_{50} (rat)] of triallate is almost one order of magnitude less (THOMPSON 1982) than its sister compound, diallate,its reported findings are still of consequence to the residue analyst. With this first



Scheme 1. Fragmentation pathway for triallate under CI conditions.

reported confirmed finding of triallate in grain pellets, the analytical chemist is now on the alert. The availability of relative retention times on various columns (R_t relative to chlorpyrifos, Ø.5Ø on OV-17 and Ø.65 on SP-21ØØ) should facilitate future identifications of triallate and hopefully avoid the reporting of its presence as a UAR.

This case history has demonstrated the intelligent sequencing of data collection as well as its simulation. As is often the case, the structural identity of a complex molecule containing N, S and Cl has been solved using only GC and low resolution mass spectral data. However, the initial GC work with selective detectors must remain as an analytical cornerstone to detect UARs for subsequent structural elucidation by GCMS.

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