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Potential Identification Problems with Carbaryl

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During surveillance analysis for pesticide residues, compounds are frequently encountered which cannot be readily identified by gas chromatographic data alone (CAIRNS & PARFITT 1980). In the past, identification was attempted using different detectors and stationary phases in the hope that the combined relative retention data acquired might correspond to an already characterized pesticide, industrial chemical, reported metabolite, breakdown compound or manufacturing impurity. Such cross correlations of relative retention data are time-consumming and rely heavily on the re-creation of the standard conditions under which the original data for comparison were formulated. Structural elucidation of unidentified analytical responses (UARs) have therefore been referred to additional analysis by gas chromatography-mass spectrometry (GCMS). These UARs must be considered as potential public health threats particularly if they are found to contain phorphorus, nitrogen, halogen or sulfur.

Recently, an extract of marionberries was found to contain an unknown organonitrogen compound at $R_t = 1.8$ (relative to parathion) on 2% DEGS at 180°C. This problem was immediately directed to GCMS and the resultant findings indicated that the compound was the insecticide, carbaryl (1-naphthyl-N-methylcarbamate). Why the routine screening methods failed in this case in identifying this common carbamate insecticide have been explored. Mass spectral characterization by chemical ionization has also indicated a unique situation which merits comment and literature exposure in the assistance of the identification of carbamates. Thermal instability of this group of insecticides had previously prompted analysis by HPLC (SPARACINO & HINES 1976).

In this paper, we now report the successful application of chemical ionization mass spectrometry with both methane and ammonia as reagent gases to characterize carbaryl for unambiguous identification in suspected residue cases where GC retention data can sometimes be inconclusive.

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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: 30 cm x 2 mm i.d. glass column packed with 2% DEGS on 80/100 mesh Chromosorb W; carrier gas and reagent gas, 30 mL methane/min; column inlet, 250°C; column temperature, 180°C, isothermal.

Sample Preparation. Sample was extracted by the Luke procedure (LUKE et al. 1975, 1981), eluted through florisil using 50% mixed petroleum ethers, concentrated to dryness using a stream of dry nitrogen and then diluted to 150 uL with methanol; 3 uL of this extract representing 1.1 g of sample was then used for analysis.

RESULTS AND DISCUSSION

The sample extract of marionberries was examined by GCMS using both methane and ammonia as reagent gases (Figure 1). As illustrated in this diagram, the elution time of 2.45 min (RRT_p = 2.1) for the UAR was extremely close to the retention time observed for the insecticide, carbaryl. This lack of exact comparison in retention data was the prime factor involved in the decision to investigate this extract via GCMS. Examination of the resultant spectra (Figure 2) revealed that the UAR was indeed the suspected carbaryl - sample and reference spectra were exactly matched. A major cause for non-correlation of retention data on GCMS was believed to be due to the large sample weight represented by the injection (about 1.1 g). It could be rationalized that such an extract could lead to a distortion in retention time via seriously overloading the stationary phase at the top of the column and thus impairing its partitioning capabilibity. Such incidences may be more common in residue analysis and emphasize the need for confirmation by mass spectrometry.

Structural elucidation of UARs has been approached in general by the use of chemical ionization techniques with various reagent gases to observe the molecular weight of the compound under investigation. Recognition of the protonated molecular ion can often narrow down the possibilities provided a comprehensive listing of pesticides, industrial chemicals, metabolites and beakdown products is available and arranged according to molecular weight (CAIRNS et al. 1981). However, this architectural approach relies on the extensive use of chemical ionization, and the subsequent

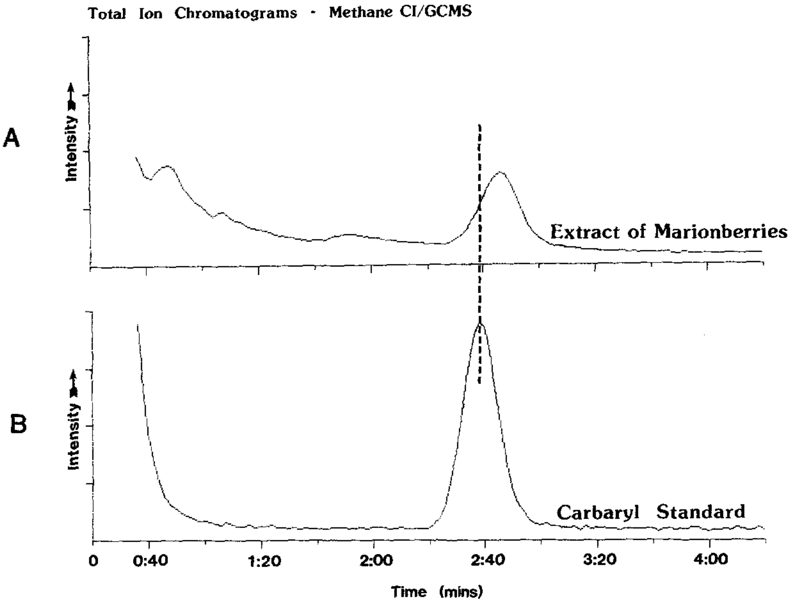


Figure 1. Total ion chromatograms (m/z 80-300) obtained using methane CI conditions of (A) sample extract of marionberries and (B) carbaryl reference standard.

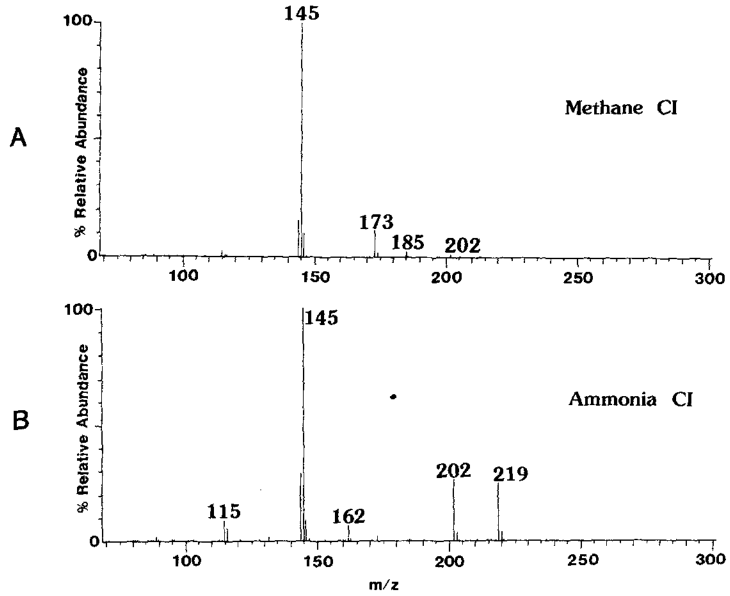
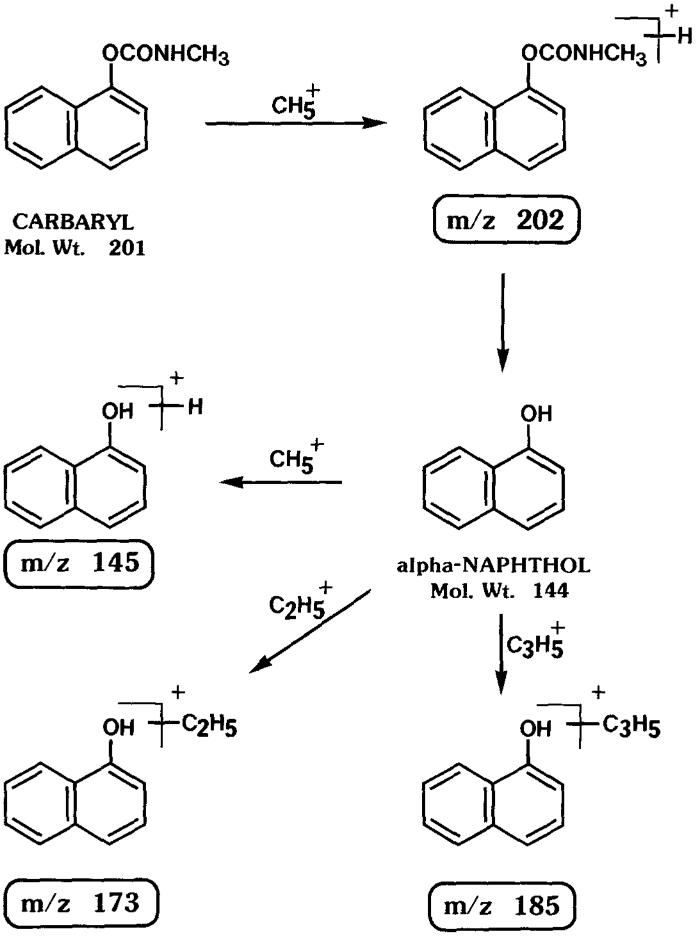


Figure 2. Mass spectra of encountered unknown analytical response of marionberries: (A) methane CI; (B) ammonia CI.

spectra obtained often yield no fragmentation whatsoever. In the case of carbamates, the suspected thermal lability of the side chain has been a problem in unambiguous identification via electron impact spectra (DAMICO & BENSON 1976; DURDEN & BARTLEY 1971). The present work reports a facile identification via the production of characteristic MH^+ ions. Mass spectral data presented in Figure 2 illustrate clearly the increased relative abundance of the MH^+ ion at *m/z* 202 when ammonia was used as reagent gas. The appearance of an ion at *m/z* 219 represents the adduct ion, $[M + NH_4]^+$. Admittedly, the relative abundance of the *m/z* 202 in spectrum A (Figure 2) is extremely low and could easily have been overlooked as insignificant. Predictive rules for chemical ionization and its fragmentation processes are not as well established as those for the more traditional electron impact studies. Obviously the use of ammonia as reagent gas (Figure 2B) was more successful in the production of a protonated molecular ion at *m/z* 202. This behavior could be rationalized in terms of the proton affinity of the NH_4^+ for carbaryl. Therefore, it is always prudent when dealing with a UAR to use several reagent gas species to maximize structural information about the molecule under examination.

In this study, however, the CI spectra revealed additional features concerning the ion-molecule reactions involved. The appearance of an ion at *m/z* 145 in both the methane and ammonia spectra could easily be attributed to the protonated naphthol structure. In previous EI studuies of carbaryl (BENSON & DAMICO 1968) the appearance of a strong ion at *m/z* 144 was reported with the base peak at *m/z* 58 coresponding to the loss of the side chain, $[CH_3\text{-}NH{=}C{=}O]^+$. Under CI conditions in the present study, the base peak was also *m/z* 58. However, it is not routine to record below *m/z* 80 because of background ions that might interfere with representative ions from the compound under study. For illustrative purposes mass spectral scans have been limited to the lower level of *m/z* 80. The issue of the production of a neutral molecule of naphthol from the initial cleavage after protonation is unusual (Scheme 1). Support for this mechanism is forthcoming from the additional evidence of adduct ions at *m/z* 173 and 185 in the case of methane and *m/z* 162 in the case of ammonia. Admittedly this proposal involves re-ionization of naphthol by CH_5^+, $C_2H_5^+$ and $C_3H_5^+$. Such events are unique and this example serves to demonstrate the possibility of ion-molecule reactions when dealing with compounds with labile side chains. The possibility of thermal decomposition followed by ionization must be discounted on the grounds that no thermal decomposition was observed either in the injection port of the GC or



Scheme 1. Proposed fragmentation pathway of carbaryl under methane CI conditions.

the compound's passage through the short column employed for the analysis. A slight possibility exists, however, in that the metal source in the mass spectrometer might induce the observed effect. On the other hand, the high source pressure employed during CI would ensure many ion-molecule collisions before the source wall was reached. This mass spectral behavior of carbaryl and other related compounds are currently under investigation to explore the exact mechanism and causes.

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