Bull. Environ. Contam. Toxicol. (1984) 32:645–650

Bulletin of Environmental Contamination and Toxicology

Dimethoate and Dimethoate Oxygen Analog in Mangoes

Thomas Cairns, E. G. Siegmund and Gregory M. Doose

Department of Health and Human Services, Food and Drug Administration, Office of the Executive Director of Regional Operations, 1521 West Pico Boulevard, Los Angeles, CA 90015

Dimethoate [O,O-dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate] is a systemic organic phosphate insecticide acaricide registered for use on a wide variety of food and feed crops. Levels permitted on human food (Code of Federal Regulations 1982) range from 0.002 ppm in milk to 2.0 ppm in various fruits and vegetables. Major dietary exposure results from residues on various fruits and vegetables. A significant degradation product via enzymatic oxidation is the oxygen analog, omethoate [O,O-dimethyl S-(N-methylcarbamoylmethyl) phosphorothioate] which is acutely more toxic than the parent compound (acute oral LD_{50} in rats for dimethoate is about 500 mg/Kg for the pure compound) and has been found to be present at final harvest (Dauterman et al. 1960; Stellar & Pasarela 1972).

Because of the questionable toxicity, high production use and potential dietary exposure, dimethoate and its oxygen analog have been included in the FDA surveillance and compliance programs (both domestic and foreign) to ensure tolerances are not exceeded. Recently the appearance of these compounds in several lots of imported mangoes analyzed in this laboratory at 0.11 ppm [via GC with flame photometric detector in the phosphorus mode (FPD-P)] constituted an unregistered use. This paper describes the analytical protocol adopted to distinguish dimethoate from its oxygen analog in an extract of mangoes to provide confirmatory evidence of the suspected unregistered use.

MATERIALS AND METHODS

All spectra were obtained on a Finnigan Model 3300 quadrupole mass spectrometer equipped with a CI source and INCOS Data System; operating conditions: 45 cm x 2 mm i.d. glass column packed with 2% DEGS on 80/100 mesh Chromosorb W; carrier gas and reagent gas for chemical ionization, 30 mL methane/min; column inlet, 180°C; column temperature, 120°C, isothermal.

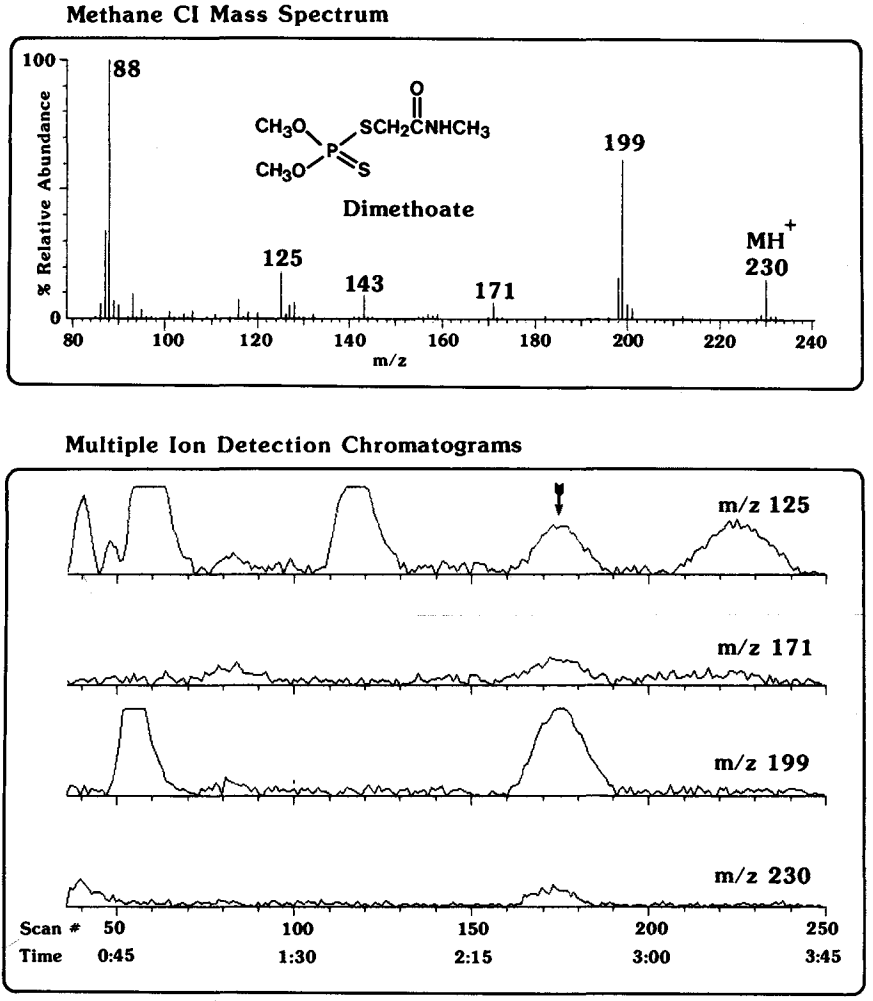
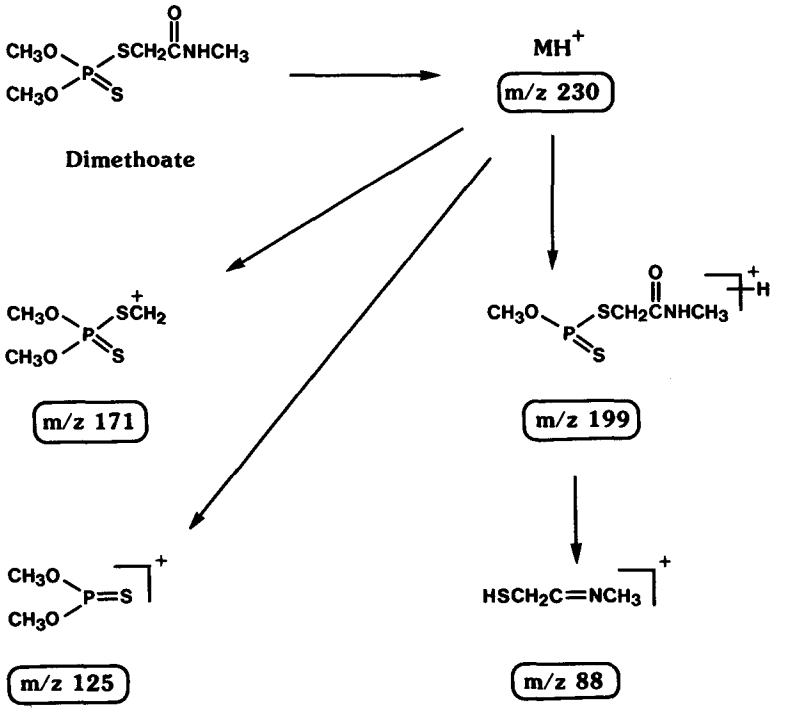


Figure 1. Chemical ionization mass spectrum of dimethoate and multiple ion detection chromatograms obtained from mangoe extract showing presence of dimethoate at scan 175.

For analysis by GCMS, 100 g portions from homogenized 10 Kg sampled lots of mangoes were extracted by the Luke procedure (Luke et al. 1981) and cleaned up using a carbon column (Luke & Doose 1983). The extract was then concentrated to 0.1 mL with a stream of dry nitrogen and 2 uL injected onto the GCMS.

RESULTS AND DISCUSSION

Since the original analyses from GC-FPD-P indicated the levels of dimethoate and its analog to be at the 0.1 ppm level, the question of level of detection by GCMS became important. Even with the extract reduction to 0.1 mL, an injection of 1 uL would constitute a loading of about 30 ng or less on column (based on 100 g sample). With this limiting criterion in mind, the selected technique was multiple ion detection (MID) of four ions from the full scan of dimethoate (Figure 1). Under methane CI conditions, dimethoate exhibited a fragmentation pathway (Scheme 1) distinctly different from that previously observed under electron impact (EI) conditions (Damico 1966). The presence of



Scheme 1. Proposed fragmentation pathway for dimethoate under methane CI conditions.

an ion at m/z 199 resulting from the loss of a methoxyl group from the protonated molecular ion [MH^+] provided a simple method to distinguish dimethoxy from diethoxy organophosphate pesticides. Loss of the methylamide side chain from MH^+ to give the ion at m/z 171 also provided a diagnostic fragment ion to characterize the dimethyl phosphorodithioate moiety. Under EI conditions (Damico

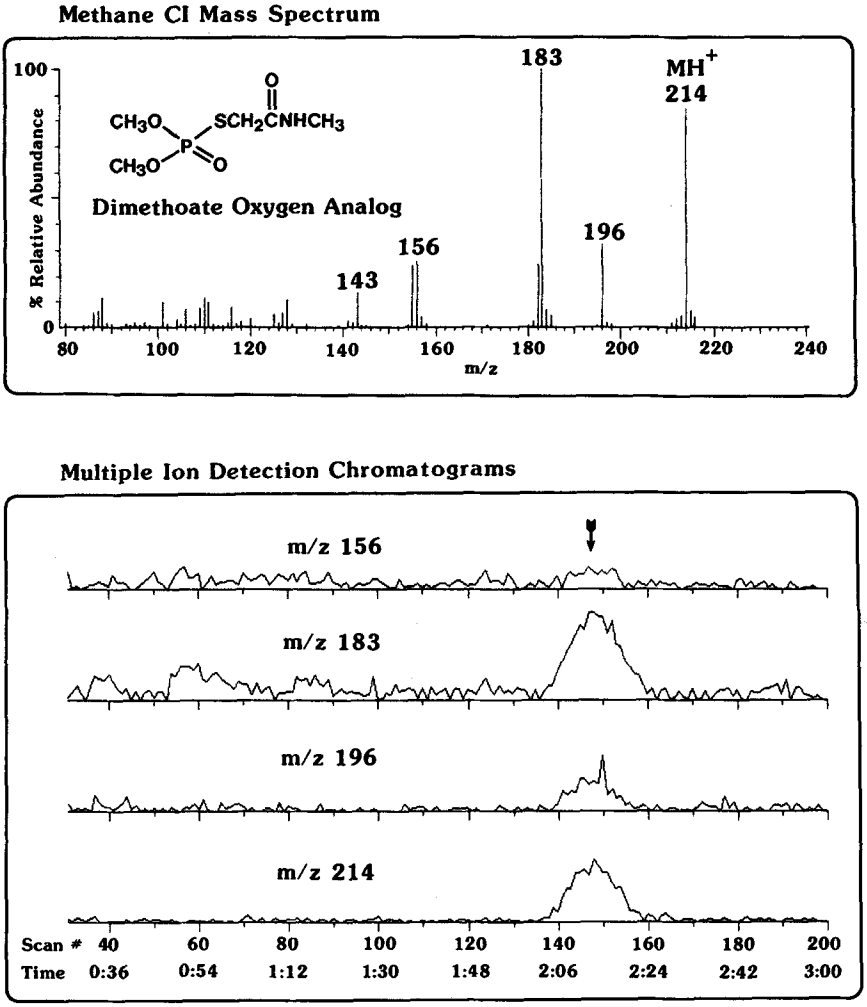
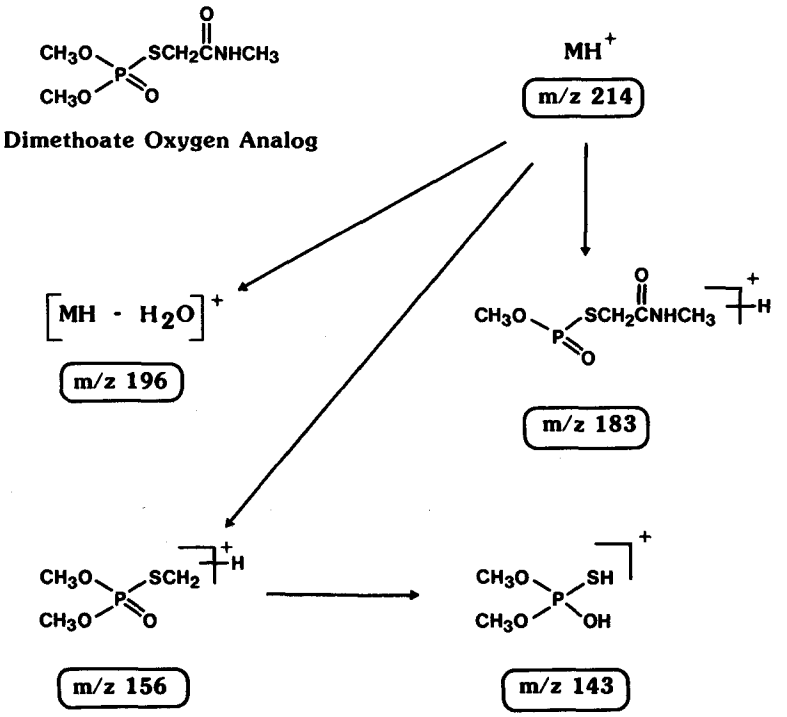


Figure 2. Chemical ionization mass spectrum of omethoate and multiple ion detection chromatograms obtained from mangoe extract showing presence of omethoate at scan 148.

1966), the general fragmentation scheme was dominated by bond cleavage between the S and C with subsequent loss of the complete side chain and proton transfer to yield dimethyl dithiophosphoric acid (m/z 158). The ion at m/z 125 is a commonly observed fragment ion encountered in both phosphorodithioates and phosphorothioates. Regarding the structure of the base peak at m/z 88, accurate mass measurements performed previously (Damico

1966) determined the ion was N-methylthioacetonitrile. For confirmation of dimethoate in the mangoes extract via GCMS-MID, the four ions selected were m/z 125, 171, 199, and 230. Figure 1 illustrates the resulting MIDs obtained, indicating the presence of dimethoate at scan 175. The four ions were detected in the correct relative abundance ratios observed for a standard reference sample. Quantitation was carried out by comparing area measurements obtained with a standard concentration injection known to be close to that for the sample (0.03 ppm dimethoate versus 0.033 ppm via FPD-P).

In the case of dimethoate oxygen analog, the mass spectral characteristics (Figure 2) resembled that discussed above for dimethoate. For example, loss of a methoxyl group from MH^+ was evident (m/z 183). However, the ion at m/z 196 representing the loss of water from MH^+ was a fragmentation not observed for dimethoate (Scheme 2). The approach to dimethoate oxygen analog



Scheme 2. Proposed fragmentation pathway for omethoate under methane CI conditions.

confirmation and quantitation was similar (Figure 2) to that employed for the parent compound (0.06 ppm omethoate versus 0.085 ppm via FPD-P).

Current trends in regulatory analysis have indicated an increased reliance on mass spectrometry notably because of the unambiguous identification it can provide. The unique role MS can play in fortifying the scientific evidence used for compliance purposes has now become an invaluable asset in the process of regulatory analysis of pesticides and their metabolites. In this particular instance, two closely related organophosphorus pesticides have been confirmed and quantitated at a concentration level below 0.1 ppm using GCMS-MID techniques to parallel the sensitivity levels normally employed in pesticide residue analysis by GC-FPD-P. This complimentary process has been illustrated to increase the reliability of results involving an unregistered pesticide use.

REFERENCES

Code of Federal Regulations (1983) 40 CFR 180.204

Damico JN (1966) The mass spectra of some organophosphorus pesticide compounds. J Assoc Off Anal Chem 49: 1027-1045

Dauterman WC, Viado GB, Casida JE, O'Brien RD (1960) Persistence of dimethoate and metabolites following foliar application to plants. J Agr Food Chem 8: 115-119

Luke MA, Doose GM (1983) A modification of the luke multiresidue procedure for low moisture non fatty products. Bull Environ Contam Toxicol 30: 110-116

Luke MA, Froberg JE, Doose GM, Masumoto HT (1981) Improved multiresidue gas chromatographic determination of organophosphorus, organonitrogen, and organohalogen pesticides in produce using flame photometric and electrolytic conductivity detectors. J Assoc Off Anal Chem 64: 1187-1195

Steller WA, Pasarela NR (1972) Gas-liquid chromatographic method for the determination of dimethoate and dimethoxon residues in plant and animal tissue, milk and eggs. J Assoc Off Anal Chem 55: 1280-1287

Received October 21, 1983; accepted January 30, 1984