important in the adsorption of neutral, polar molecules. Adsorption on the hydrated cations was considered one of the main adsorption mechanisms of parathion, *p*-nitrophenol, and phenol by montmorillonite (Saltzman and Yariv, 1975; Saltzman and Yariv, 1976). Fripiat and Dondeyne (1960) demonstrated that the bonding energy of water on the kaolinite surface proper is much lower than the hydration energy of the ions. Namely, at the lower moisture contents where the largest increase in the rate of hydrolysis was observed upon a small addition of water, this water probably is sorbed mostly as ligand water of the cations. These ligand water molecules associated with the exchangeable cations may be the hydrolysis sites for the organophosphates studied. The dependence of the hydrolysis kinetics on the cation (Figure 2 and Table III) further supports this suggestion. In the solid systems used, the catalytic site could also be the fixation site of the phosphate decomposition product. This appears so because the movement of the hydrolysis products for any distance on the dry surface would be extremely slow, whereas the fixation to degradation ratio being independent of time suggests that the fixation step is rapid and not limiting. The nature of the alkyl thiophosphate and the fact that fixation occurs only after hydrolysis suggests that fixation and decomposition occur also at locations in the adsorbed organophosphate that are close to each other or even identical. This identity or proximity of the degradation and fixation sites together with the direct effect of the exchangeable cation on the fixation discussed above (aside from its effect on the degradation rate) supports again the proposal that the cation and its hydration shell may be the hydrolysis site. Infrared studies are being conducted in an attempt to obtain direct evidence for this assumption.

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Field Desorption Mass Spectrometry of Commercial Pesticides and Mixtures of Pesticides

Hans-Rolf Schulten

Highly polar pesticides that are used as insecticides, acaricides, fungicides, and herbicides have been investigated with low- and high-resolution field desorption mass spectrometry. By use of defined sample amounts, standard field desorption emitters, a controlled time/temperature program for desorption, and photographic detection, the potential of the method for qualitative and semiquantitative analyses of commercial pesticides and mixtures of pesticides has been demonstrated. The high molecular ion intensities displayed, the strongly reduced fragmentation, and the sensitivity and analytical resolution obtained indicate that field desorption is particularly well suited for the investigation of mixtures. Furthermore, desorption of a synthetic combination of a parent pesticide, *p,p'*-DDT, and five of its metabolites yielded almost exclusively molecular ions of the different constituents of the mixture. Interaction of the various components of the mixtures in field desorption was remarkably small and did not prevent the identification of the individual components.

The utility of field desorption mass spectrometry (FDMS) for the analyses of compounds of low volatility has been demonstrated for a wide variety of substances (Beckey and Schulten, 1975a,b). The first application of the method to environmental chemicals showed that bridged polycyclic chlorinated pesticides and some of their metabolites yield high molecular ion intensities and little or no fragmentation as compared to other ionization methods in mass spectrometry such as electron impact (EI) and chemical ionization (CI) (Schulten and Beckey, 1973a). The basic advantages of the FD technique, namely small sample consumption, high sensitivity, and strongly reduced thermal degradation (no evaporation is required in FDMS), make it particularly applicable to the detection and identification of metabolites and/or nonmetabolic decomposition products (Schulten et al., 1973). In addition to pesticides and pesticide metabolites mutagenic, cocarcinogenic, and antiseptic substances have been the subject of preliminary FD investigations (Schulten, 1973). The results obtained underline the utility of the technique

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for the study of single model compounds.

Actual analytical problems, however, usually involve determination of different chemical species in sometimes complex mixtures. Thus, the analytical resolution (i.e., the ability to resolve and determine individual components of a mixture) of a mass spectrometric technique appears to be the controlling factor for its use in mixture analysis. In considering this objective, we have examined the capacities of FDMS by applying it to the analysis of pesticides in three different *kinds of mixtures*: (a) as commercial products containing a parent pesticide and sometimes accompanying impurities; (b) as commercially available mixtures of different pesticides; and (c) as a synthetic mixture of a parent pesticide and five of its metabolites and/or decomposition products.

EXPERIMENTAL SECTION

The FD spectra were produced on a modified CEC 21-110B instrument (Schulten and Beckey, 1973b) using the photographic detection system with vacuum evaporated AgBr plates. The resolution obtained was better than 15 000 (at half-peak width), and the average accuracy in the mass determination was ±2 millimass units. Field desorption emitters used in all experiments were prepared by high-temperature activation of 10 μm diameter tungsten wires (Beckey et al., 1973). The distribution and morphology of the produced microneedles were as shown previously (Schulten and Beckey, 1972). FD emitters with an average length of 30 μm for the carbon microneedles were used as standards. The ionization efficiency was calibrated in the field ionization mode. In general, a sample amount of 1×10^{-7} g was applied to the standard emitter via the syringe technique (Beckey et al., 1970). The desorption (and exposure) time of the adsorbed compound was regulated with an automated emitter heating device (Schulten and Nibbering, 1976) at a threshold of 2×10^{-8} A for the total emission (measured between the field anode and the slotted cathode plate at 2 mm distance and at +10/−2 kV accelerating voltage). The recorded mass range extended from m/e 17 to 560.

Although the data processing is tedious and the dynamic range limited, the photoplate as an integrating recording system allowed cumulative recording of the spectra obtained during fractionated desorption (i.e., desorption consecutively of each individual component of the mixtures at its respective best anode temperature). In all cases the spectra allowed molecular weights and elemental formula to be established, and the presence of fragment ions due to direct bond cleavages provided considerable assistance in the identification of pesticides and pesticidal metabolites.

The following commercial products and mixtures were studied by FDMS: (a) commercial products of single pesticides—endosulfan, captan, 2,4-dinitro-6-methylphenol, diazinon, and dodine; (b) commercial pesticide mixtures—carbaryl and tetradifon; 2,4-D sodium salt and MCPA sodium salt; (c) synthetic mixture—combination of *p,p'*-DDT and five of its metabolic or degradation products.

RESULTS AND DISCUSSION

(a) Commercial Pesticides. (I) *Bridged Polycyclic Chlorinated Hydrocarbons.* Commercially available endosulfan (thiodan) containing 90–95% of the α and β isomers was investigated with FDMS (Figure 1). The molecular ion of the insecticide at m/e 403.817 ($C_6H_6O_3Cl_6S$) was the base peak of the FD spectrum. This is in contrast to the EIMS (Safe and Hutzinger, 1973), which showed the molecular ion with about 5% relative intensity. Furthermore, a multiplicity of fragmentation processes

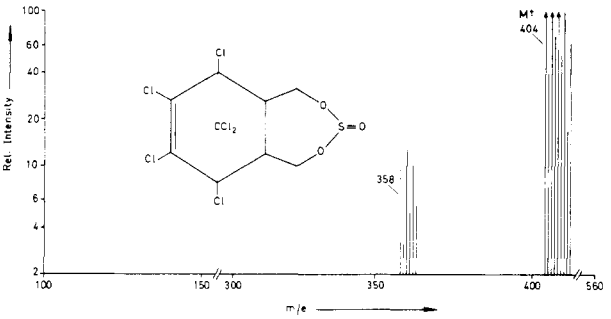

Figure 1. FDMS of endosulfan (1,4,5,6,7,7-hexachloro-5-norbornene-2,3-dimethanol cyclic sulfite, 91–93% active substance), solvent acetone, BAT 6–8 mA.

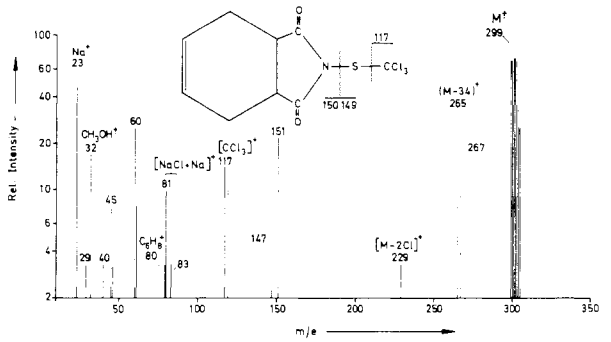

Figure 2. FDMS of captan (*N*-(trichloromethylthio)tetrahydrophthalimide, 91% active substance), solvent methanol, BAT 8–12 mA.

such as (M − Cl), (M − SO), and (M − (Cl + S)), etc. was found that are completely missing in the FD mass spectrum in Figure 1. No ions were observed between m/e 60 and the molecular ion group, with the exception of those at m/e 358 to m/e 364. The characteristic isotope cluster and precise mass measurements indicate that these signals are due to thiodandiol (1,2,3,4,7,7-hexachloro-5,6-bis(hydroxymethyl)bicyclo[2.2.1]hept-5-ene), the initial substance used in the production of endosulfan. Since the technical product was treated as an unknown in the desorption process, i.e. the emitter temperature was raised automatically by an electronic device with a constant increase of the emitter heating current from 0 to 30 mA within 10 min desorption time (exposure time of one trace on the photoplate), saturated blackening resulted for the signals of endosulfan at m/e 404, 406, 408, and 410. Therefore, only qualitative detection of thiodandiol was possible by FDMS. The percentage of thiodandiol present in the commercial sample was determined by chemical methods and found to be approximately 4%.

(II) *Phthalic Acid Derivatives.* Figure 2 shows the spectrum of a commercial fungicide, captan, when field desorption is performed under the same experimental conditions as described for endosulfan. Again the base peak of the spectrum is assigned to the molecular ion, which is at m/e 298.934 ($C_9H_8O_2NCl_3S$). A best anode temperature (BAT) has been defined (Winkler and Beckey, 1972) as the temperature of the field desorption emitter at which predominantly molecular ions are generated and thermally field induced fragmentation is reduced. The BAT for captan is characterized for direct heating of the emitter by the heating current, in this case 8 mA according approximately 80 °C (Kümmler and Schulten, 1975). The ion production observed above BAT, i.e. between 8 and 30 mA, leads to a number of fragmentation processes of the sample molecules on the surface of the emitter. The prominent signal at m/e 151 is due to a direct bond

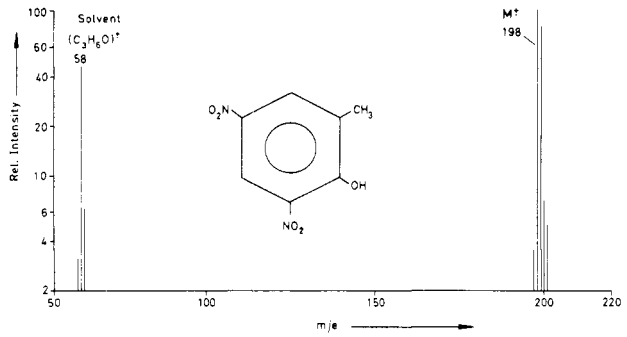

Figure 3. FDMS of 2,4-dinitro-6-methylphenol, 80–82% acid equivalent, solvent acetone, BAT 0 mA.

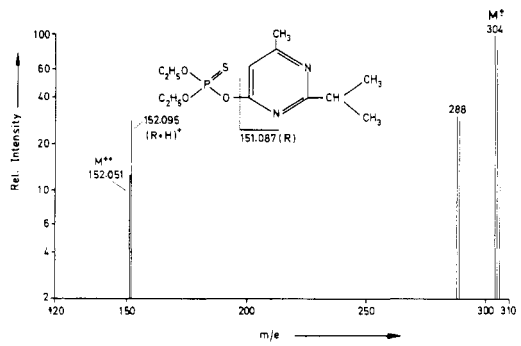

Figure 4. FDMS of diazinon (*O,O*-diethyl *O*-[(2-isopropyl-4-methyl)-6-pyrimidyl]thiophosphate, 95–96% active substance), liquid sample, BAT 0–2 mA.

cleavage between the nitrogen and the sulfur atom following or coincident with proton transfer to the basic center of the molecule. The probable proton donor (apart from intermolecular transfer) is the solvent, methanol, which exhibits an ion at *m/e* 32.026 but not the usually observed intense $(M + H)^+$ ion. The occurrence of tetrahydrophthalimide in the FD mass spectrum is confirmed by precise mass measurements (*m/e* 151.063, $C_8H_9O_2N$). The entire other part of the captan molecule (149 mass units) is not observed, but the peaks at *m/e* 117–119 clearly indicate the CCl_3 group. Since this fragment is also detected in the FD mass spectra of other pesticides containing the trichloromethyl function such as kelthane, trichlorphon, and *p,p'*-DDT (Schulten, 1973) this terminal cleavage apparently is a more general feature of the FDMS of these compounds. In addition, signals of small relative abundance are recorded at *m/e* 229 for (M – 2Cl) and a fragment of the cyclohexene ring at *m/e* 80.063 (C_6H_8).

The peaks in the upper mass range at 265–267 are explained by the presence of an impurity in the commercial phthalimide fungicide. High-resolution mass measurements indicate that this accompanying compound contains one less chlorine and one more hydrogen atom than captan. The FD spectra of the captan standard and the analogous compounds folpet and difolatan which were obtained from samples of high purity (99.9 ± 0.2%) did not show the loss of 34 mass units. This substantiates our conclusion that the ions at *m/e* 265–267 (Figure 2) resulted from an impurity. In addition to captan, its fragments, and this impurity, two more compounds could be identified in the commercial pesticide. First, relatively weak peaks at *m/e* 333, 335, and 337 are due to an exchange of hydrogen with chlorine and are thought to represent an impurity from the chlorination process. Second, the intense signal found for sodium clearly indicated an accompanying inorganic substance. The cluster ion for sodium chloride was found at *m/e* 80.948 $(Na^{35}Cl + Na)^+$ and *m/e* 82.945 for $(Na^{37}Cl + Na)^+$. Calibration measurements were made and the percentage of this inorganic impurity was estimated from the FD spectra to be 0.5–2%. Volumetric analysis of the commercial product revealed that indeed about 1.5% free chloride $(Cl)^-$ is present. To the best of the author's knowledge, the FD spectrum in Figure 2 is the first mass spectrum that displays an intact cluster ion for an inorganic salt as well as the intact parent molecule of an organic pesticide with high relative intensity in one mass spectrum. (Very recently similar results have been reported for inorganic salts and sulfonates (commercial dyestuffs) by Schulten and Kümmler (1976).)

(III) *Aromatic Nitrophenol Compounds.* The outstanding characteristic of FDMS, namely its high molecular ion intensities, is demonstrated in Figure 3. The spectrum of the herbicide 2,4-dinitro-6-methylphenol showed a typical FD mass spectrum that enabled straightforward interpretation. The base peak is formed by the molecular ions at *m/e* 198.028 ($C_7H_6O_5N_2$). In addition, only two groups of signals appeared for water $(H_2O)\cdot^+$, $(H_3O)^+$, and for the solvent acetone, at *m/e* 58–59. During the desorption process, the sample produced the highest total emission values at room temperature. The BAT in this case is 20–30 °C and the emitter heating current 0 mA. There were no alkali metal ions or any other impurities detected. In the analysis of relatively volatile compounds such as this, FDMS is limited in examining thermally induced fragmentation because desorption occurs before enough thermal energy can be transferred to induce fragmentation (Schulten et al., 1973). If the information about the molecular weight is not sufficient and structural information is desired the analysis of these relatively volatile compounds by other methods for ionization, e.g., electron impact, chemical ionization, or field ionization (FI), may be more useful.

(IV) *Organophosphorus Pesticides.* The FDMS of diazinon, a contact insecticide and acaricide, in Figure 4 is useful for high-resolution studies. The precise mass determination of the molecular ion at *m/e* 304.101 was performed with an error of only 0.5 mmu ($C_{12}H_{21}O_3N_2PS$). The ions at *m/e* 288–289 are probably due to the molecular ions of an accompanying compound, diazoxon. The occurrence of this oxygen analogue of diazinon in the commercial product is supported by accurate mass measurements and low-resolution FDMS of a sample of diazinon of analytical purity (99.8 ± 0.2%). These spectra displayed the ions shown in Figure 4 with high relative abundances but no signal at *m/e* 288–289. At the nominal mass 152 a doublet is recorded. One peak, accurate mass 152.051, is produced by the doubly charged molecular ion. The second signal, accurate mass 152.095, has the elemental composition $C_8H_{12}ON_2$ and is formed by the direct bond cleavage between the oxygen and phosphorus atoms. Protonation generates 2-isopropyl-4-methyl-6-hydroxypyrimidine, a very useful fragment for structural information of a major moiety of the parent molecule. The direct cleavage at the glycosidic (Schulten and Games, 1974) and phenolic (Schulten and Beckey, 1974a) oxygen, together with proton transfer, has been observed in a large number of FD spectra and represents another general characteristic of FDMS.

(V) *Organic Salts.* One particularly important feature of FDMS is its capacity for the analysis of organic and inorganic salts (Schulten and Röllgen, 1975a, and references cited therein). As an example we report in Figure 5 the FD spectrum of the fungicide dodine. As might be expected from the previous investigation on the formation of ions in FDMS of salts no molecular ion is detected.

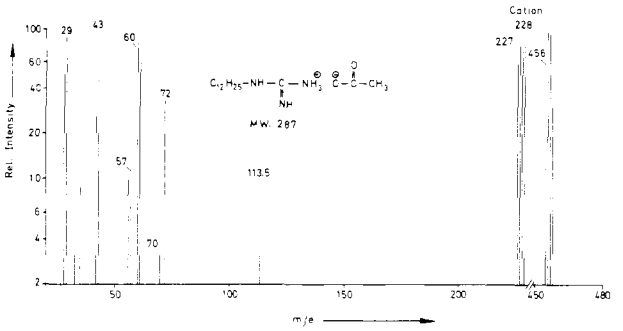

Figure 5. FDMS of dodine (*N*-dodecylguanidine acetate, 99% active substance), solvent methanol, BAT 15 mA.

Similarly as in the studies of quaternary ammonium salts (Brent et al., 1973), alkali salts of bile acids (Games et al., 1974), and other onium substances (Sammons et al., 1975; Röllgen and Schulten, 1975; Wood et al., 1975; Schulten and Röllgen, 1975b) the cation appears with high relative abundances. The *N*-dodecylguanidinium ion at *m/e* 228.244 ($C_{13}H_{30}N_3$) is the base peak. However, *N*-dodecylguanidine is displayed with comparable intensity at *m/e* 227.236 and yields a doubly charged ion at *m/e* 113.618. In view of the pronounced signal for acetic acid at *m/e* 60.021 and protonated acetic acid at *m/e* 61.029 it is assumed that most of the protons are transferred to the anionic moiety of the salt, although a weak signal (8% log. blackening) for the guanidinium ion at *m/e* 60.056 (CH_6N_3) is found. Furthermore, an intense peak at *m/e* 455.480 ($C_{26}H_{59}N_6$) indicates a novel type of ion in FDMS resulting from cationization (Röllgen and Schulten, 1975) of *N*-dodecylguanidine by the *N*-dodecylguanidinium ion. In addition a very weak cluster ion consisting of two cations and one anion at *m/e* 515 and a number of fragments from the alkyl part of the dodine molecule is detected.

(b) Mixtures of Commercial Pesticides. A mass spectrometric method producing predominantly molecular ions and strongly reduced fragmentation should be well suited for the analysis of mixtures. In fact it has been demonstrated for line products of antibiotics (Rinehart et al., 1974), crude extracts of bile acids (Games et al., 1976), and a combination of a parent drug with some of its metabolites (Schulten, 1974) that, in the application of FDMS, one focal point is the investigation of mixtures. Since in practice pesticides are often used as mixtures that consist of different effective environmental chemicals we have examined some of these composed products with the FD technique.

(I) *Carbamates.* A widely used pesticidal mixture that is commercially available consists of the insecticide carbaryl and the acaricide tetradifon. The FD mass spectra of standards of the individual components were compared to the FD spectrum of this mixture. In Figure 6 the FD mass spectrum of carbaryl is shown. The molecular ion at *m/e* 201.079 ($C_{12}H_{11}O_2N$) is the base peak. This is in contrast to the results obtained with EIMS, giving 5% relative intensity and FIMS where 50% relative intensity for this ion is reported (Damico et al., 1969). A prominent signal at *m/e* 143 is due to the direct bond cleavage at the naphtholic oxygen; proton transfer leads to 1-hydroxynaphthalene (*m/e* 144). This is the base peak in EIMS and is displayed with 80% relative intensity in FIMS. The high-resolution FDMS of carbaryl reveals a doublet at nominal mass 58. The upper mass at *m/e* 58.042 (C_3H_6O) is assigned to the solvent acetone, and the lower mass at *m/e* 58.029 (C_2H_4ON) gives information about the other part of the carbaryl molecule. It is often observed in FDMS that direct bond fission, particularly on the linking heteroatom, proton transfer, and field ionization yield both charged complementary parts of the examined substance molecule, thus enabling straightforward and easy interpretation. Direct cleavage of the molecule into two charged particles is a considerable advantage for mass spectrometric analysis.

The intense doubly charged ion at *m/e* 101.043 for $(M + H)^{2+}$ (and no M^{2+} signal) is consistent with the criteria described recently (Schulten and Beckey, 1974b) for distinguishing between $M^{\cdot+}$ and $(M + H)^+$ ions. Further, doubly charged ions are recorded for 1-hydroxynaphthalene at mass 72.029 $(C_{10}H_8O)^{2+}$. These ions are useful in confirming the right assignment of the singly charged species in the FD spectrum (Schulten et al., 1973).

The second component of the mixture, tetradifon, a relatively volatile substance, showed no fragmentation in its FD spectrum (Figure 6a). Since the $M^{\cdot+}$ and $(M + 1)^+$ ions produce saturated blackening on the photoplate, the (M + 3) ion was chosen as base peak. In addition to the molecular group only two doubly charged ions were recorded at *m/e* 177 M^{2+} and 178 $(M + 2)^{2+}$ with very low relative intensity.

The FD spectrum of the mixture of carbaryl and tetradifon is given in Figure 6c. The integrating recording of the photoplate is practically adding up the spectra of the single compounds shown in Figures 6a and 6b. In the mixture, the sample molecules of carbaryl and tetradifon desorb consecutively according to their best anode temperature (in the mixture), i.e. fractionated desorption occurs. No interference between the two compounds is observed. However, to give an example that the conditions of FDMS for mixture analysis are not always so ideally fulfilled we have studied a commercial mixture of two pesticides that are salts.

(II) *Chlorinated Aromatic Pesticides (Salts).* The mixture consisted of 2,4-D sodium salt and MCPA sodium salt, a technical product used as herbicide. As expected the molecular ions of the salt are not detected with FDMS, but the FD spectrum of MCPA sodium salt (99.8 ± 0.2%) in Figure 7a exhibits very intense cluster ions $(M_A + Na)^+$ and $(2M_A + Na)^+$ from which the molecular weight of the intact salt (cation plus anion) can easily be derived. Strong signals are found for $(Na^{35}Cl + Na)^+$ at *m/e* 80.948 and $(CH_3COONa + Na)^+$ at *m/e* 104.993 and the appropriate isotope peaks. The sodium chloride apparently is an impurity of the line product; the origin of sodium acetate is not yet clear. As noted above, direct bond cleavage at the phenolic oxygen and proton transfer leads to *m/e* 142.018 ($C_7H_7O^{35}Cl$) and gives diagnostic information about the substituted aromatic part of the molecule. In addition the free substituted acetic acid at *m/e* 200 is produced in a solvolysis reaction as previously observed for sodium acetate (Schulten and Röllgen, 1975a). Although it is difficult to interpret the signal at *m/e* 211, precise mass measurements confirm the structure given in Figure 7a. Since it can be excluded that this compound, 2-methylphenoxyacetic acid sodium salt, is a major impurity of the MCPA herbicide it is assumed that the loss of chlorine from the para position is a field process on the surface of the field anode. Two facts support this assumption. First, there is a pronounced relative abundance of the signal at *m/e* 211 (equal to that of the base peak at *m/e* 245 for $(M_A + Na)^+$) and, second, this sodium cluster ion forms an ion species that is recorded at *m/e* 433 and is due to cationization of the parent molecule $(M_A + 211)^+$. In the light of these findings it is clear that FDMS investigations of pure standards are necessary to determine whether a technical product contains an im-

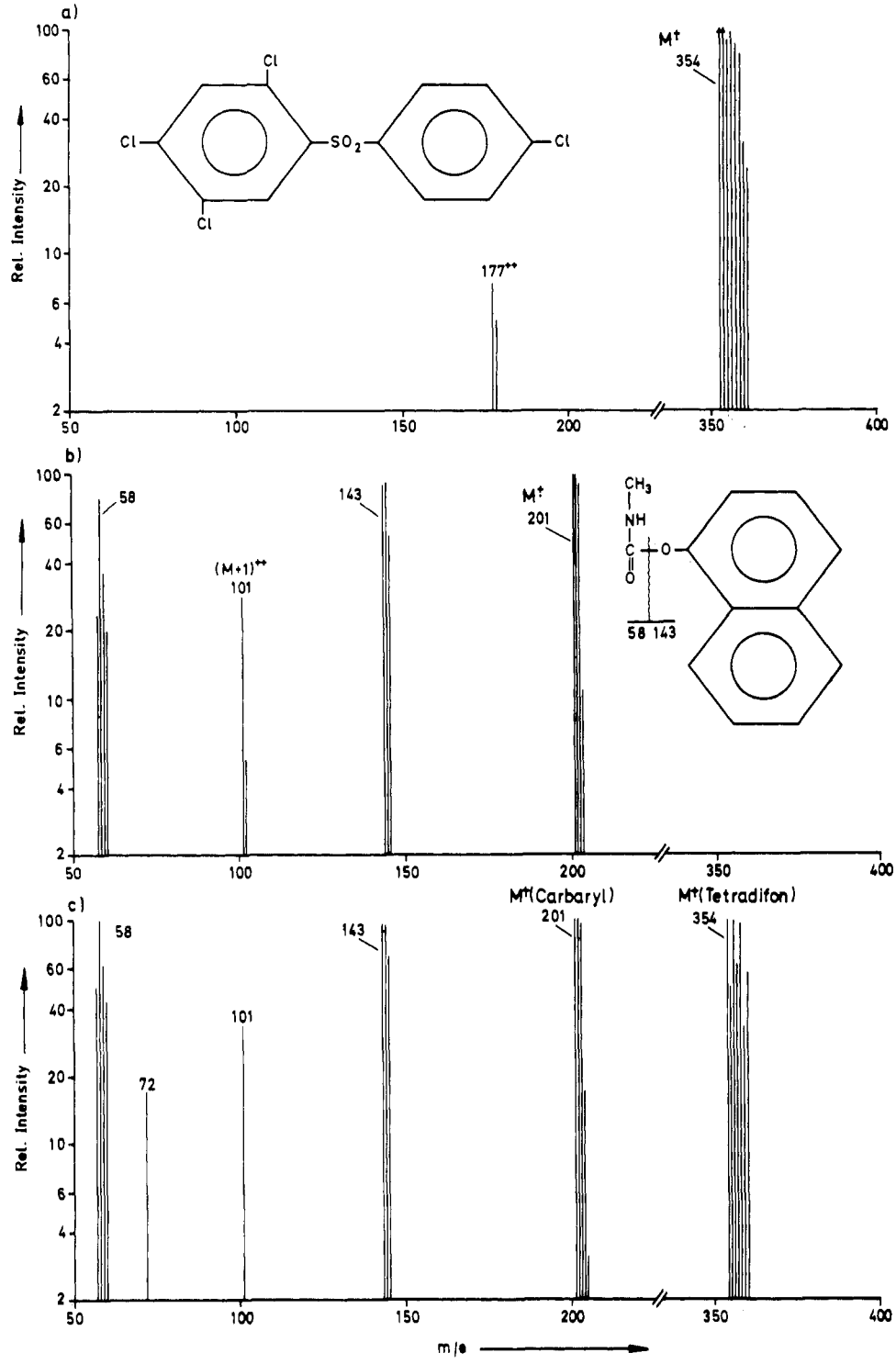

Figure 6. (a) FDMS of tetradifon (3,4,6,4'-tetrachlorodiphenylsulfone, 98-99% active substance), solvent acetone, BAT 6 mA. (b) FDMS of carbaryl (1-naphthyl-*N*-methylcarbamate, 99% active substance), solvent acetone, BAT 8-12 mA. (c) Commercial mixture of 50% carbaryl and 13% tetradifon, solvent acetone; the best total emission is observed between 8 and 15 mA.

purity or not. In our first approach analyzing commercial pesticides by FDMS we have therefore restricted our discussion about impurities to chemical species that were identified unambiguously by other analytical methods.

The FD mass spectrum of 2,4-D salt (99.9 ± 0.2%) in Figure 7b resembles the general features of the MCPA spectrum. The 2,4-dichlorophenol at m/e 162 is clearly detected. Furthermore, the loss of one and two chlorine atoms from the aromatic moiety of the 2,4-D salt leads to the cluster ions at m/e 197 and 231, respectively. The most informative peaks for the cluster ions of $(M_A + Na)^+$ and $(2M_A + Na)^+$ are easily discerned by their typical isotope pattern, mass measurements, and predominant intensity. Again the parent molecule is cationized by the monochlorophenoxyacetic acid sodium cluster (m/e 231) to generate the group of peaks at m/e 473 ff. At m/e 323-325 a novel type of ion in FDMS is generated by cationization of the parent molecule M_B by an inorganic cluster ion of sodium chloride $(Na_2Cl)^+$.

The FDMS of the 1:1 mixture of the 2,4-D and MCPA sodium salts is shown in Figure 7c. This spectrum is obtained under the same experimental conditions as the

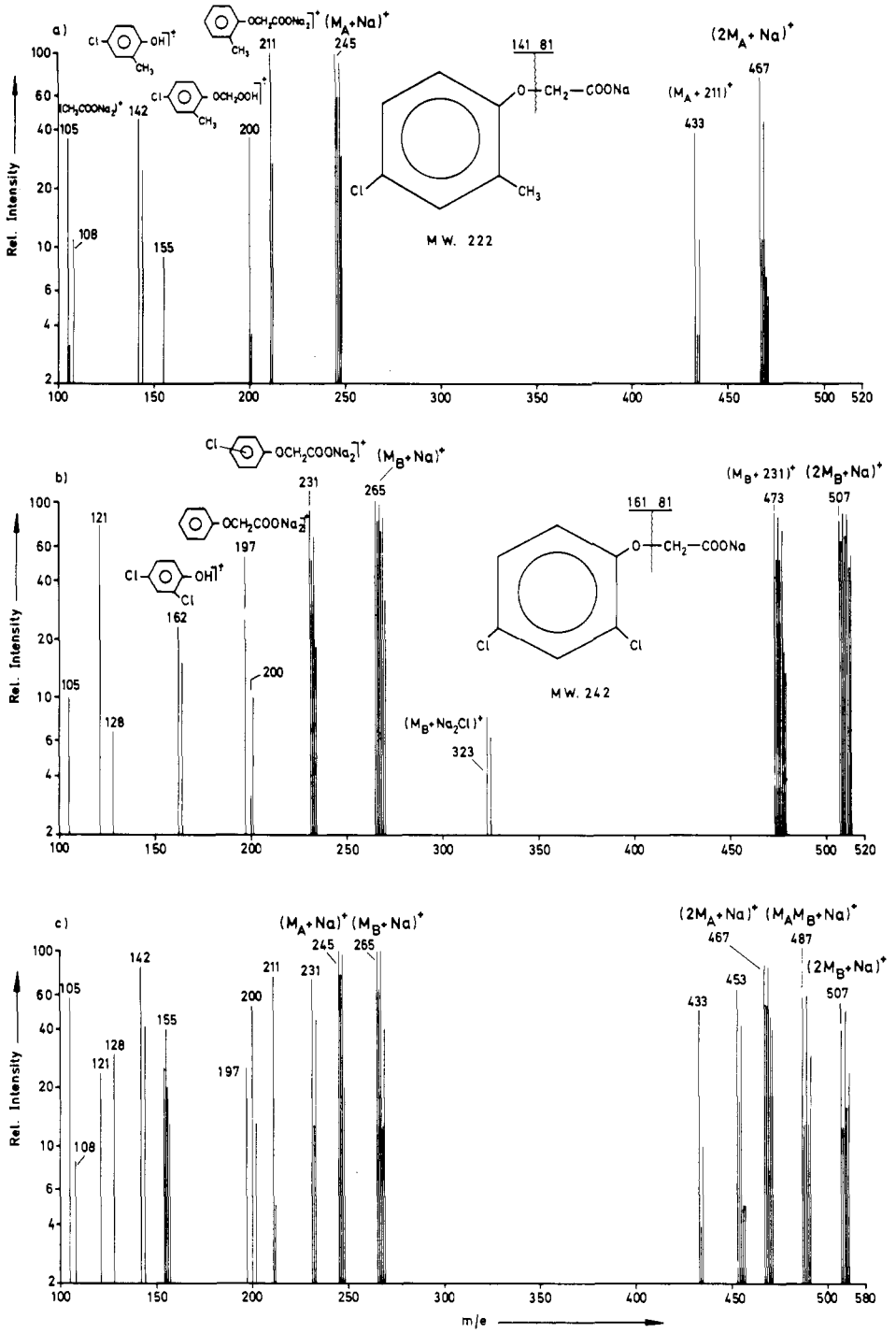

Figure 7. (a) FDMS of MCPA (2-methyl-4-chlorophenoxyacetic acid sodium salt), solvent water, BAT 15-18 mA. (b) FDMS of 2,4-D (2,4-dichlorophenoxyacetic acid sodium salt), solvent water, BAT 20-23 mA. (c) FDMS of bi-hedonal (50% 2,4-dichlorophenoxyacetic acid sodium salt and 50% 2-methyl-4-chlorophenoxyacetic acid sodium salt), solvent water; the best total emission was observed between 15 and 25 mA.

FD spectra for the individual compounds, i.e., the emitter heating current is raised constantly by an automatic device from 0 to 30 mA. Principally, the FD spectrum of the mixture displays all essential signals that were observed for the single components. Taking into account that ionization and desorption occur from the solid, adsorbed layer on the emitter surface, there is at least qualitative agreement of the spectra in Figures 7a and 7b with the spectrum of the mixture in Figure 7c. This agreement indicates promise for the application of FDMS in mixture analysis. Careful calibration studies will be necessary to prove whether the method is in general feasible for quantitative investigations. There are considerable shifts in the relative intensities, changes in the ratios of protonated and unprotonated species, and mixed cluster ions (e.g., $(M_AM_B + Na)^+$) observed in the example given in Figure 7. However, it has been demonstrated in a preliminary study using stable isotope dilution that quantitation of a drug (cyclophosphamide-d_0 or -d_6) is possible within ±5% when a sample amount of ~100 ng was consumed for one FD measurement (Schulten, 1976).

Mixtures of Pesticides and Pesticide Metabolites. Except for a preliminary attempt to identify by FDMS a parent drug and some of its metabolites in a test mixture without derivatization (Schulten, 1974) little is known about the potential of the method in mixture analysis of

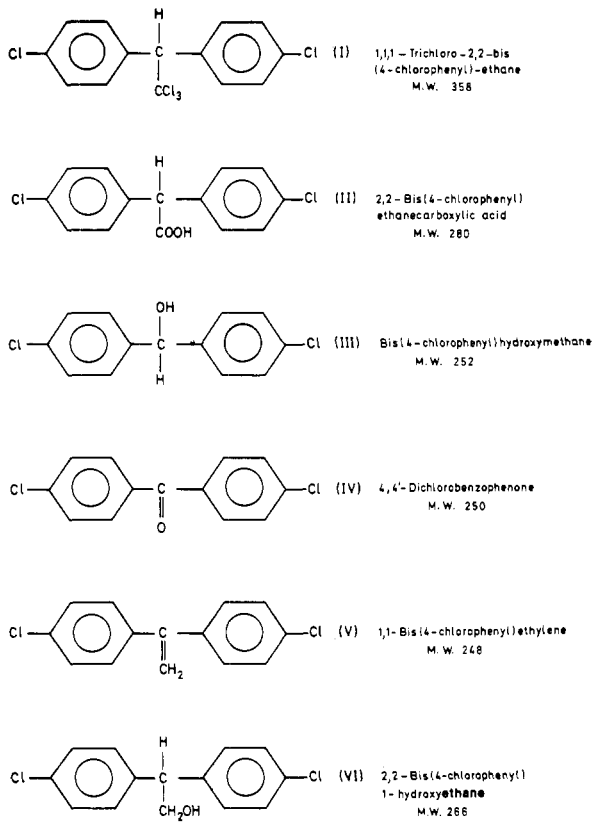

Figure 8. Structure, nomenclature, and molecular weight of *p,p'*-DDT and some of its metabolites and nonmetabolic decomposition products.

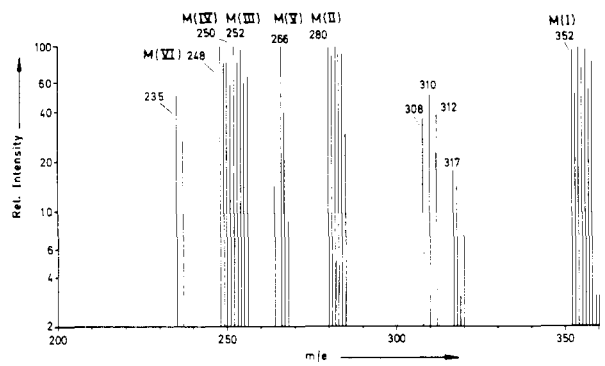

Figure 9. FDMS of a synthetic mixture of the substances I–VI, solvent acetone, concentration ~10^{-3} M; the best total emission is observed between 5 and 12 mA.

compounds of a wide polarity range. In order to explore the analytical resolution of the FD technique for a combination of a parent pesticide and some of its metabolites or nonmetabolic decomposition products we have prepared a mixture of *p,p'*-DDT (I) and the substances II–VI (Figure 8). The FDMS of this synthetic mixture of pure substances is shown in Figure 9. The spectrum consists almost exclusively of the molecular ions of the individual components. Accurate mass measurements allowed the determination of the molecular weight with an average error of ±2 millimass units. In view of the small sample required (10^{-9}–10^{-6} g adsorbed on the FD emitter) and the high sensitivity the method is well suited for the analysis of crude or partially purified extracts of pesticides and pesticide metabolites.

CONCLUSION

In summarizing the results from commercial, single pesticides of different classes of substances and with a wide variety of chemical functions, the FD method reveals considerable capacities not only for molecular weight determination but also for yielding information about the structure of completely unvolatile substances. Since large organic salts as such are in general not amenable to other ionization techniques FDMS widens substantially the scope of applicability of mass spectrometric analysis.

For the analytical application of FDMS there are two most promising fields: the analysis of organic and inorganic salts, and the analysis of mixtures of compounds within a wide range of polarity. Therefore, it is expected that FDMS will play a major role as a tool in the analysis of pesticides, mixtures of pesticides, and associated metabolic products.

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Persistence of Endrin in Indian Rice Soils under Flooded Conditions

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A radiotracer study was conducted to determine the relative persistence of endrin-^{14}C under flooded conditions in eight Indian rice soils. Endrin decomposed rapidly and reached low levels within 55 days in all soils except in a sandy soil. Interestingly, most rapid degradation occurred in pokkali soil despite its high salt content. The decrease in the total radioactivity partitioned in the chloroform–diethyl ether fraction was less pronounced despite the rapid decline in endrin levels indicating the formation of stable metabolites. Radioautography revealed that endrin was converted to six stable metabolites in all soils except in sandy and kari soils; five compounds were detected in kari soil and three compounds in sandy soil. More rapid degradation of endrin occurred in nonautoclaved samples of three soil types than in autoclaved samples indicating microbial participation in its degradation. The addition of rice straw enhanced the degradation of endrin. Liming the acid soils had no effect on the degradation rate of endrin.

Endrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene), a chlorinated hydrocarbon insecticide, is highly effective against common rice insects. Its widespread use in agriculture has caused serious environmental hazards leading to its restricted use in several countries. Such restricted use of endrin could adversely affect the recent intensified efforts to increase food production in developing countries such as India, because substitutes for endrin are costly and often not very effective. Information concerning its fate and persistence in Indian rice soils under flooded conditions is, therefore, both useful and necessary.

Chlorinated hydrocarbon insecticides persist for several years in soils under nonflooded conditions (Edwards, 1972; Pionke and Chesters, 1973). In contrast, some of these chlorinated hydrocarbons such as benzene hexachloride (1,2,3,4,5,6-hexachlorocyclohexane), DDT (1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane), methoxychlor (1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane), and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,5,5a-tetrahydro-4,7-*endo*-methanoindene) readily break down in a predominantly anaerobic flooded soil ecosystem (Sethunathan, 1973a). Although the degradation of endrin in soil and aquatic systems and by microorganisms isolated from soil, fresh water, lake bottom sediments, and marine environments has been demonstrated (Patil et al., 1970, 1972; Guenzi et al., 1971; Matsumura and Boush, 1971), information on its fate and behavior in flooded soils is rather limited. In one instance, endrin was shown to persist in 3 out of 4 Philippine rice soils under flooded conditions (Castro and Yoshida, 1971). A radiotracer study was therefore conducted to determine the relative persistence of endrin in Indian rice soils including two organic acid sulfate saline soils under flooded conditions.

MATERIALS AND METHODS

Soils. Some of the characteristics of the soils used in this study are listed in Table I. Among the soils used, two saline acid sulfate soils from Kerala, South India, are unique rice soils of extreme acidity and locally known as kari and pokkali soils (Bloomfield and Coulter, 1973).

Labeled Endrin. Uniformly labeled endrin-*1,2,3,4,10*-^{14}C (specific activity, 7.44 mCi/mmol; 98% purity) was obtained from Mallinckrodt, Science Products Division, Radiochemical Department, St. Louis, Mo. The labeled endrin was dissolved in hexane (100 ml) after evaporating off the benzene carrier. An aliquot of the stock solution was evaporated to dryness and the residues were redissolved in ethanol prior to incorporation into the soils.

Soil Incubation Studies. The soils (20 g) were placed in test tubes (200 × 25 mm diameter). Labeled endrin was introduced to the soils in ethanol (0.1 ml) together with 0.5 mg of 95% technical endrin as carrier. The total radioactivity added to the soils was 113×10^4 cpm/20 g of soil. The soils were then flooded with distilled water (25 ml) and incubated at room temperature (28 ± 4 °C). At intervals, two replicate tubes were removed for analysis.

Effect of Rice Straw. Only alluvial soil from the Institute farm was used in this study. The soil (20 g) was thoroughly mixed with rice straw powder ground to pass through 100 mesh screen at 0.5% (w/w) level in test tubes (200 × 25 mm). The labeled endrin was introduced to the soils in ethanol (0.1 ml) with technical endrin (0.5 mg), and after 3 h the soils were flooded with distilled water (25 ml). At intervals, two replicate tubes were removed for analysis.

Effect of Liming. Alluvial soil from the experimental farm of Central Rice Research Institute and kari soil (20 g) were thoroughly mixed with 25 mg and 600 mg of $CaCO_3$, respectively, in test tubes. The labeled endrin was introduced to the soils in ethanol (0.1 ml) with 0.5 mg of technical endrin and, after 3 h, the soils were flooded with distilled water (25 ml). At intervals, two replicate tubes were removed for residue analysis.

Effect of Soil Autoclaving. A laterite and two alluvial soils were used. The soils (20 g) in the test tube (200 × 25 mm) were moistened with 5 ml of distilled water and autoclaved for 1 h at 15 psi on three alternate days. Labeled endrin in ethanol (0.1 ml) with technical endrin (0.5 mg) was introduced. After 3 h, the soils were flooded with distilled water (25 ml). At intervals, two replicate tubes were removed for residue analysis.

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